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THE SERIES SPECTRA OF TWO-VALENCE-ELECTRON ATOMS OF PHOSPHORUS (P_{IV}), SULPHUR (S_V), AND CHLORINE (Cl_{VI})

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ABSTRACT

Series spectra of two-valence-electron atoms of P, S, and Cl.—In a previous paper,[1] the regular and irregular x-ray doublet laws were used to predict the spectra of stripped atoms, that is, atoms having only one valence electron. The method has now been applied to the spectra of two-electron atoms, since, although these spectra consist of triplets or singlets instead of doublets, the same laws apply to them. In this way 23 lines of P_{IV} have been identified, 17 lines of S_V and 6 lines of Cl_{VI}. With the help of the Ritz equation, 12 term values of P_{IV} and 8 of S_V were also determined. In a table are collected all known term values for two-electron atoms of Mg, Al, Si, P and S.

Physical significance of the x-ray irregular doublet law.—Spectral lines which give parallel curves on a Moseley diagram $\sqrt{\nu/R}$ plotted as a function of atomic number) and which therefore follow this law, are produced by jumps between orbits of the same total quantum number but with different screening constants.

I. INTRODUCTION

THE present paper is merely a further illustration of the fecundity of the method for the identification of spectral lines which we have recently brought to light. This method grows out of the discovery that both the regular and the irregular x-ray doublet laws are also applicable throughout the whole field of optics[1] so long as a series of atoms of like electronic structure but varying effective nuclear charge is under observation. The irregular doublet law makes possible the prediction of the precise position of a particular line, while the regular doublet law foretells the character of its fine structure, i.e. the frequency separation of its components.

We have heretofore used the irregular doublet law only to predict the positions of lines belonging to a stripped-atom series, i.e. the series constituted by the stripped atoms of Li, Be, B, C, N, or of Na, Mg, Al,

[1] Bowen and Millikan Phys. Rev. **24**, 209 (1924)

Si, P, S, Cl. Such a series may be called a one-electron series since it has but one valence electron, which radiates as it jumps between the series of levels characteristic of the second quantum state of the lithium group or the third quantum state of the sodium group.

In the present paper we apply the same method to a two-electron system (one having two electrons in its outer shell). The irregular doublet law is here applicable precisely as in the case of the one-electron system. But while a one-electron system is characterized by lines the fine structure of which is a doublet, a two-electron system is characterized by a fine structure consisting of either triplets or singlets. Since, however, we have shown that the regular or relativity doublet law holds for triplets as well as for doublets, it is possible to predict with its aid the frequency separation of any two of the three lines of a triplet, and we have in this paper chosen for this purpose the two extreme lines, in this respect changing the procedure followed in a preceding paper in which we worked with the two more widely separated adjacent lines instead of the outside ones. In other words, we are now using the p_1p_3 separation where we before used the p_1p_2 separation.

2. Significance of the Irregular Doublet Law

Before applying the irregular and regular doublet laws to the actual identification of lines produced by two-electron systems, it will be of interest to present the proof that whenever the frequency of a given spectral line is found to progress linearly with atomic number, i.e. to follow the irregular doublet law, this line must be produced by a jump between orbits of the same total quantum number.

The simple Moseley law

$$\frac{\nu}{R}=\left(\frac{Z-\sigma}{n}\right)^2$$

shows that when there is a jump between two orbits of different screening constants σ_1 and σ_2 and of total quantum numbers n_1 and n_2 the frequency ν' produced by a jump between these orbits is given by the difference between two expressions of the foregoing form, viz.

$$\frac{\nu'}{R}=\left(\frac{Z-\sigma_1}{n_1}\right)^2-\left(\frac{Z-\sigma_2}{n_2}\right)^2$$

or

$$\frac{\nu'}{R}=\frac{(n_2^2-n_1^2)Z^2-2(n_2^2\sigma_1-n_1^2\sigma_2)Z+n_2^2\sigma_1^2-n_1^2\sigma_2^2}{n_1^2\,n_2^2}.$$

This equation shows at once that if ν' is to vary linearly with Z the coefficient of Z^2 in the first term must be zero, i.e. that n_2 must equal n_1.

If n_2 is not equal to n_1 the first term introduces a variation of ν' with Z^2. In other words, *the irregular doublet law signifies that there is a difference in screening constant between orbits of the same total quantum number.*

Since the irregular doublet law also is equivalent to parallelism between the lines on the Moseley diagram corresponding to the two sets of levels the differences between which determine the irregular doublet, it follows that whenever such parallelism is found the levels between which it exists correspond in every case to the same total quantum number.

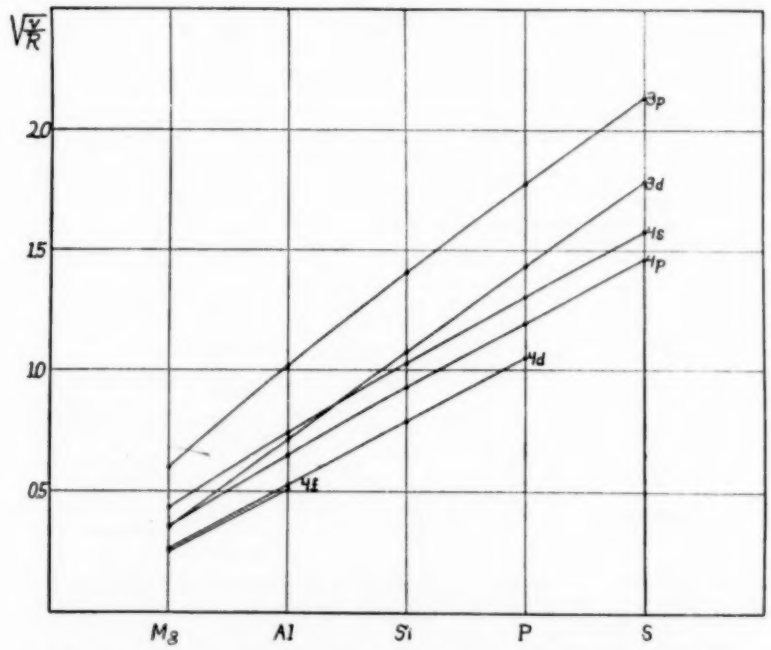

Fig. 1. Series spectra of two-valence electron atoms from Mg_I to S_V.

All the relations in this section are nicely illustrated by the Moseley diagram shown in Fig. 1, in which all the parallel lines have the same total quantum number while those corresponding to different total quantum numbers have definitely different slopes.

3. Lines and Term Values for P_{IV}, S_V, and Cl_{VI}

With the aid of the irregular and regular doublet laws the lines and term values for P_{IV}, S_V, and Cl_{VI} have been obtained as follows.

According to Fowler[1] the first term of the diffuse series of Mg_I has a wave-length at $\lambda = 3838.29$ and a frequency in vacuum of 26045.9.

[1] Fowler, Series in Line Spectra, p. 116.

According to Paschen[3] the corresponding line of Al_{II} has a wave-length $\lambda = 1724.95$ and a frequency 57972.7. According to Fowler[4] the corresponding line of Si_{III} has a wave-length $\lambda = 1113.76$, which corresponds to the frequency 89786.0. These three frequencies constitute an approximately linear progression (irregular doublet law) as shown in Table I,

TABLE I

Irregular doublets

	$3p_1 - 3d$ ν	Diff.		$4s - 4p_2$ ν	Diff.
Mg_I	26045.9		Mg_I	6650.4	
		31926.8			7502.73
Al_{II}	57972.7		Al_{II}	14153.13	
		31813.3			7700.37
Si_{III}	89786.0		Si_{III}	21853.5	
		30993.9			7802.0
P_{IV}	120779.9		P_{IV}	29655.5	
		30017.8			7850.9
S_V	150797.7		S_V	37506.4	
	$3S - 3P$ ν	Diff.		$4p_1 - 4d$ ν	Diff.
Mg_I	35051.4		Mg_I	6340.2	
		24793.7			9672.42
Al_{II}	59845.1		Al_{II}	16012.62	
		23033.8			10250.18
Si_{III}	82878.9		Si_{III}	26262.8	
		22311.5			10224.1
P_{IV}	105190.4		P_{IV}	36486.9	
		21953.6			
S_V	127144.0				
		21805.2			
Cl_{VI}	148949.2				

which should yield a frequency difference between Si_{III} and P_{IV} of about 31000 (see Table I), and this difference locates the first term of the diffuse series of P_{IV} at a frequency value of about 121,000, i.e., at wave-length $\lambda = 826$ A. We should then find a strong phosphorus triplet

TABLE II

Regular doublets

	$3p_2 - 3p_1$ $\Delta\nu$	$Z - s$	s
Mg_I	60.81	4.870	7.130
Al_{II}	187.3	6.451	6.549
Si_{III}	394.	7.769	6.231
P_{IV}	696.3	8.958	6.042
S_V	1128.1	10.106	5.894
Cl_{VI}	1720.1	11.230	5.770

[3] Paschen, Ann. der Physik **71**, 544 (1923)

[4] Fowler, Nature **113**, 802 (1924)

at about this wave-length. Our plates revealed just such a strong triplet at λλ823.21, 824.76, and 827.95 (see Table III).

The regular doublet law (Table II) gives a progression of the separations of the most distant components which can be computed from the

TABLE III

Series lines for PIV

Int.	λ(I. A., vac.)	ν	Δν$_p$	Δν$_d$		Term values	
2	631.74	158293.0			$3p_1-4s$	$4s$	187687.9
5	823.21	121476.4			$3p_2-3d$	$5s$	105479.2
			> 228.6				
6	824.76	121247.8			$3p_2-3d$		
			> 467.9			$3p_1$	345964.9
6	827.95	120779.9			$3p_1-3d$	$3p_2$	346432.8
						$3p_3$	346661.4
4	1025.58	97506.0					
4	1028.13	97264.2				$4p_1$	157825.3
4	1030.53	97037.1			pp' group	$4p_2$	157973.7
4	1033.14	96792.4				$4p_3$	158032.4
4	1035.54	96567.9					
3	1484.55	67360.5			$3d-4p_1$	$3d$	225185.0
			> 149.6				
3	1487.85	67210.9			$3d-4p_2$	$4d_1$	121330.7
			> 58.8			$4d_2$	121338.4
2	1489.16	67152.1			$3d-4p_3$	$4d_3$	121344.0
0	1904.97	52494.3			$4p_2-5s$		
			> 147.9				
0	1910.35	52346.4			$4p_1-5s$		
4	2725.67	36688.2			$4p_3-4d_3$		
4	2729.61	36635.3	58.2	> 5.3	$4p_2-4d_2$		
3	2730.00	36630.0			$4p_2-4d_3$		
5	2740.13	36494.6			$4p_1-4d_1$		
			148.4	> 7.7			
3	2740.71	36486.9			$4p_1-4d_2$		
				> 5.3			
*		36481.6					
6	3348.67	29862.6			$4s-4p_1$		
			> 148.4				
6	3365.39	29714.2			$4s-4p_2$		
			> 58.7				
5	3372.06	29655.5			$4s-4p_3$		
10	950.66	105190.4			$3S-3P$		

* Not observed.

values of s for MgI AlII SiIII in the last column, at about $\Delta\nu = 700$, correct to about ± 20. *The observed $\Delta\nu$ is 696.5, in altogether satisfactory agreement with the prediction.*

The location of SV could now be predicted from the sequence of differences in Table I, the PV−SIV difference being at once seen to be

necessarily about 30,000 and therefore the frequency of S_V to be 150,800, with an uncertainty of say 200, which corresponds to a wave-length uncertainty of 1 angstrom. This definitely identified our strong line at λ663.14, $\nu = 150797.7$ as the $3p_1 - 3d$ line of S_V. The regular doublet law of Table II then predicted the separation of the extreme components of the $3p - 3d$ triplet shown in Table IV, with an uncertainty of ± 20 frequency units (0.1A).

TABLE IV

Series lines for S_V

Int.	λ(I. A. vac.)	ν	$\Delta\nu$		Term values	
1	437.37	228639.4		$3p_3 - 4s$	$4s$	273075.0
			427.9			
1	438.19	228211.5		$3p_2 - 4s$		
			757.8		$3p_1$	500497.7
1	439.65	227453.7		$3p_1 - 4s$	$3p_2$	501252.4
					$3p_3$	501618.2
3	658.25	151918.2		$3p_3 - 3d$		
			365.8		$4p_1$	235191.6
4	659.84	151552.4		$3p_2 - 3d$	$4p_2$	235480.7
			754.7		$4p_3$	235568.6
4	663.14	150797.7		$3p_1 - 3d$		
4	849.25	117751.1			$3d$	349700.0
4	852.19	117345.0				
5	854.81	116985.6		pp' group		
4	857.83	116573.2				
4	860.46	116216.9				
1	873.20	114521.3		$3d - 4p_1$		
			321.7			
1	875.66	114199.6		$3d - 4p_2$		
4	2639.68	37883.4		$4s - 4p_1$		
			289.1			
2	2659.98	37594.3		$4s - 4p_2$		
			87.9			
1	2666.21	37506.4		$4s - 4p_3$		
6	786.51	127144.0		$3S - 3P$		

The corresponding Cl_{VI} line should fall at a frequency of 180,000 (λ555 A), but this triplet should be of weak intensity and this particular region is so studded with Cl and O lines, some of them strong, that certain identification upon our plates is practically hopeless.

These $3p - 3d$ lines were determined for P_{IV} by measurement in the 1st, 2nd, 4th, and 7th orders, and for S_V in the 1st, 2nd, 3rd, 8th, and 9th orders.

The location of the $4p_1 - 4d$ and $4s - 4p_3$ lines for P_{IV} and S_V is made in precisely the same way with the aid of the irregular doublet law for $4p_1 - 4d$ and $4s - 4p_3$, as shown in Table I. In this table the $4p_1 - 4d$ lines are taken from Fowler[2] for Mg_I and from Paschen[3] for Al_{II}. This gave

the first difference in the $4p_1-4d$ sequence of Table I. From this difference we were able to identify the triplet λλ3791.13, 3796.18, 3806.60 given by Sawyer and Paton[5] as the $4p_1-4d$ Si_{III} triplet, which when reduced to vacuum gives the frequency 26262.8 shown in Table I.

The $4s-4p_3$ term for Si_{III} was found in the same way to correspond to the Sawyer-Paton triplet $\lambda_{air}=4552{,}50,\ 4567.66,\ 4574.66$, which yields the vacuum frequency 21853.5 shown in the table.

The addition to this frequency of the nearly constant difference 7800 fixes unambiguously our strong line $\nu=29655.5$ as $4s-4p_3$ for P_{IV} (see Table III), and a similar procedure identifies at once the strong sulphur triplet shown in Table IV as $4s-4p$ for S_V, and also fixes the third member of this triplet λ2666.21, $\nu=37506.4$, as $4s-4p_3$. The consideration of the intensities of these particular triplet lines combined with the irregular

TABLE V

Series lines for Cl_{VI}

Int.	λ(I. A., vac.)	ν	
3	724.13	138096.8	
3	727.54	137449.5	
4	730.31	136928.2	pp' group
3	733.89	136260.2	
3	736.76	135729.4	
4	671.37	148949.2	$3S-3P$

doublet law is quite sufficient for their identification, though they may also be checked with the aid of the regular doublet law, as used above with the $3p_3-3p_1$ separations (Table II). It is only in the case of the S_V triplet here considered that certain irregularities in the progressions raise in our minds a little question as to the certainty of the identifications.

The exceedingly strong $3S-3P$ singlet lines in Tables III, IV, and V are indubitably fixed by their intensities and the exceedingly uniform progression that the irregular doublet law exhibits for these lines as shown in Table I.

Thus far the irregular doublet law has been our most certain guide, but it fails us entirely for the identification of the $3p-4s$ triplets because these represent jumps between levels of different total quantum numbers and such jumps have been shown above not to follow this law. We actually identified these lines easily in S_V by the agreement of their frequency differences with those of the $3p-3d$ triplet, for $3p-4s$ should be the next strongest line to $3p-3d$, having the same frequency difference.

[5] Sawyer and Paton, Astrophys. J. **57**, 290 (1923)

In the case of P_{IV} only one component of the $3p-4s$ line is shown because the others are obscured on our plates by other strong lines. This was, however, the only unidentified phosphorus line below 750 A and further its position could be predicted within two or three angstroms by comparisons of the sequence of $3p_1-4s$ lines in stripped atoms with the corresponding lines in two-valence-electron atoms.

The $4p-5s$ lines in P_{IV} were identified by a precisely similar comparison aided by the fact that the separation here was of necessity the same as in $4s-4p$.

The $3d-4p$ triplet has its position exactly predicted by the fact that $(3d-4p)+(3p-3d)=(3p-4s)+(4s-4p)$ and all these except the first are already found.

TABLE VI

Comparison of term values

	$N=$	3	4	5
	$R/N^2=$	12192.78	6858.44	4389.40
s	Mg/1		20474.5	9799.3
	Al/4		15147.3	7942.64
	Si/9		12962.5	7096.0
	P/16		11730.5	6592.5
	S/25		10923.0	
p_1	Mg/1	39760.5	13820.0	7419.0
	Al/4	28570.3	11598.17	6535.34
	Si/9	24097.7	10522.5	
	P/16	21622.8	9864.1	
	S/25	20019.9	9407.7	
d	Mg/1	13714.7	7479.5	4704.1
	Al/4	14078.41	7595.02	4760.18
	Si/9	14121.4	7604.4	
	P/16	14074.1	7583.2	
	S/25	13988.0		
f	Mg/1		6994.8	4469.0
	Al/4		7109.90	4603.27
f'	Al/4			4419.45

The pp' group of lines that appear in Table III, IV, and V have been found with the indicated wave-lengths in the extreme ultraviolet. Precisely similar pp' groups have been previously found by Paschen and Götze[6] in Mg_I and Al_{II} and they were therefore to be expected in Si_{III}, P_{IV}, S_V, and Cl_{VI}, since these are all atoms of the same electronic structure.

In the case of the spectra of stripped atoms such as those with which we have been dealing in preceding papers, we have been able to start

[6] Paschen-Götze, Seriengesetze der Linienspectren, Julius Springer (1922)

with a circular orbit remote enough from the nucleus so that its term value could be computed at once from the corresponding term value in hydrogen. The identification and measurement of the lines then fixed all the other reported term-values. In the present case the f and f' terms were not in our data and resort had therefore to be made to the usual method of finding the absolute values of some particular terms through the aid of the Ritz equation.[7] The foregoing series of lines then gave all the rest of the term values recorded in Tables III and IV.

For convenience of reference and comparison we have exhibited in Table VI all of our series terms for these two-valence-electron atoms in the form adopted in a preceding article for our series of stripped atoms. As indicated, the actual term values have been divided for the purposes of this table by the square of the numbers 1, 2, 3, 4, 5. The $3p_1$ value for silicon in this table was taken from Fowler's computation.[4] The other silicon values were obtained from this and our own data combined with that of Sawyer and Paton[5] mentioned above. In the case of phosphorus, Table III, the lines above 2000 A were taken from Geuter.[8]

As will be seen from Fig. 1, the spectra of these two-valence-electron atoms follow the Moseley law quite as well as we have before shown those of the stripped atoms to do.

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[7] Fowler, Report on Series in Line Spectra.
[8] Kayser, Spektroskopie, vol. VI, p. 246.

THE SERIES SPECTRA OF THREE-VALENCE-ELECTRON ATOMS OF PHOSPHORUS (P_{III}), SULPHUR (S_{IV}), AND CHLORINE (Cl_V)

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Abstract

Series spectra of three-valence-electron atoms of P, S and Cl.—By the methods of the preceding paper, 21 lines of P_{III} have been identified, 20 lines of S_{IV} and 10 lines of Cl_V, including a pp' group for each; also 10 term values of P_{III} have been determined and 10 term values of S_{IV}, including the x level.

Screening constants for one, two, and three valence electron systems are collected in a table for Na to Cl. The values increase regularly with the number of valence electrons and decrease with the atomic number, the difference decreasing as the atomic number increases.

HAVING obtained the characteristic lines and term values for stripped or one-valence-electron atoms from Na_I through Cl_{VII}, and then for two-valence-electron atoms from Mg_I through Cl_{VI}, we now apply the same methods to three-valence-electron atoms and seek the series lines of the atoms Al_I through Cl_V. These lines, according to Sommerfeld's rule, must be doublets.

As heretofore, the first predictions grow out of the irregular doublet law shown in Table I, in which both Al_I and Si_{II} are obtained from

TABLE I

Irregular doublets

	$3p_1-3d$ ν	Diff.		$4s-4p_1$ ν	Diff.
Al_I	32324.69		Al_I	7601.57	
		46731.31			8090.03
Si_{II}	79056.0		Si_{II}	15691.6	
		37265.1			7849.6
P_{III}	116321.1		P_{III}	23541.2	
		34868.1			8524.0
S_{IV}	151189.2		S_{IV}	32065.2	
		33200.4			
Cl_V	184389.6				

	$4p_1-4d$ ν	Diff.
Al_I	5967.76	
		13804.84
Si_{II}	19772.6	
		11143.7
P_{III}	30916.3	
		10757.5
S_{IV}	41673.8	

Fowler.[1,2] The difference between these two frequencies as shown in Table I fixes the position of P_{III} at 850A within say 50A. This falls into the region of the strongest phosphorus lines found, namely, the lines λ855.65 and λ859.69, and the separation of these two lines is seen in Table II to fit nicely into the progression exhibited by the regular doublet

TABLE II

Series lines of P_{III}

Int.	λ(I.A., vac)	ν	Δν		*Term values*	
2	848.65	117834.2		$3p_2-4s$	$4s$	125497.8
			559.4			
3	852.70	117274.8		$3p_1-4s$	$5s$	67292.8
4	855.65	116870.6		$3p_2-3d$		
			549.5		$3p_1$	242772.5
6	859.69	116321.1		$3p_1-3d$	$3p_2$	243332.1
4	913.99	109410.7			$4p_1$	101821.2
5	917.14	109035.2	559.8		$4p_2$	101957.8
5	918.69	108850.9	559.2	pp' group		
5	921.86	108476.0				
					$3d_1$	126450.0
5	998.03	100197.1		$3p_2-x$	$3d_2$	126461.4
			559.7			
5	1003.64	99637.4		$3p_1-x$	$4d$	70904.5
1	2420.47	41314.3		$x-4p_1$		
			136.4		x	143135.1
1	2428.49	41177.9		$x-4p_2$		
5	2884.75	34665.0		$4p_2-5s$		
			136.6			
5	2896.17	34528.4		$4p_1-5s$		
6	3220.23	31053.7		$4p_2-4d$		
			137.4			
6	3234.54	30916.3		$4p_1-4d$		
4	4058.53	24639.5		$3d_2-4p_1$		
6	4060.41	24628.1	136.8	$3d_1-4p_1$		
7	4081.18	24502.7		$3d_2-4p_2$		
7	4223.34	23677.9		$4s-4p_1$		
			136.7			
7	4247.87	23541.2		$4s-4p_2$		

law (see Table V). The corresponding line in sulphur is fixed with certainty as the strong doublet λ657.34, λ661.42. Quite similarly from Table I the corresponding line in chlorine is fixed at λ538.08 and λ542.33.

The next doublet to be expected with the same frequency separation as $3p-3d$ is $3p-4s$. The appearance of this separation in the doublet at

[1] Fowler, Report on Series in Line Spectra, 156—(Al)
[2] Fowler Nature **113**, 802 (1924)—(Si)

λ848.65, λ852.70 for P_{III} suggests such an identification, and further its position was predicted by comparison of the $3p-4s$ lines in two-valence-electron atoms. This also located the $3p_2-4s$ line shown in S_{IV}, the other component of which is obscured by the complex oxygen line at 554 A (see Table III).

Just as the pp' group in the two-valence-electron system was early recognized by its striking structure as well as through showing the characteristic $3p$ separation, so here the same two characteristics identified the pp' group listed under P_{III}, S_{IV}, and Cl_V (Tables II, III, and IV).

This same separation identified the $3p-x$ doublet for P_{III} and S_{IV}, the level from which the electron jumps being here denoted x because it cannot be fitted into either the s or the d series of levels. Fowler found

TABLE III

Series lines of S_{IV}

Int.	λ(I.A., vac)	ν	$\Delta\nu$		Term values	
2	551.17	181432.2		$3p_2-4s$	$4s$	200109.2
5	657.34	152127.8	938.6	$3p_2-3d$	$5s$	110531.0
6	661.42	151189.2		$3p_1-3d$		
					$3p_1$	380591.2
5	744.92	134242.8			$3p_2$	381541.4
5	748.40	133618.6	950.5			
5	750.23	133292.3	950.0	pp' group	$4p_1$	167824.0
5	753.76	132668.6			$4p_2$	168034.0
4	809.69	123503.9	950.1	$3p_2-x$	$3d_1$	229400.0
5	815.97	122553.8		$3p_1-x$	$3d_2$	229414.3
2	1108.36	90223.1	206.2	$x-4p_1$	$4d$	126151.6
2	1110.90	90016.9		$x-4p_2$		
					x	258037.5
0	1623.62	61590.7		$3d_2-4p_1$		
2	1624.00	61576.4	210.7	$3d_1-4p_1$		
2	1629.20	61380.0		$3d_2-4p_2$		
0	1739.03	57503.3	210.5	$4p_2-5s$		
1	1745.42	57292.8		$4p_1-5s$		
2	2387.72	41881.0	207.2	$4p_2-4d$		
3	2399.59	41673.8		$4p_1-4d$		
5	3098.36	32275.1	209.9	$4s-4p_1$		
3	3118.65	32065.2		$4s-4p_2$		

these x levels in Si_{II} and C_{II}, which are also three-valence-electron systems.

Similarly, the irregular doublet law of Table I fixed the positions of $4s-4p_2$ and $4p_1-4d$ lines and the equality of their doublet separations confirmed the identification.

The $3d-4p$ lines were obtained from the equation

$$(3p-3d)+(3d-4p)=(3p-4s)+(4s-4p),$$

and the $x-4p$ lines from

$$(3p-x)+(x-4p)=(3p-3d)+(3d-4p).$$

TABLE IV

Series lines of Cl_V

Int.	λ(I.A., vac.)	ν	Δν	
3	538.08	185846.0		$3p_2-3d$
			1456.4	
4	542.33	184389.6		$3p_1-3d$
2	564.30	177210.7		
2	565.47	176844.0	1507.0	
2	569.14	175703.7	1500.8	pp' group
2	570.31	175343.2		
6	629.33	158899.1		
6	633.18	157933.0	1495.6	
6	635.31	157403.5	1497.3	pp' group
5	639.24	156435.7		

The identification is again confirmed by the fact that these doublets all show the $4p$ separation (see Tables II and III). The $4p-5s$ doublet was identified just as was the $3p-4s$ doublet. In the case of S_{IV} there is a very slight uncertainty about the correct identification of $4p-5s$ because of the existence of two pairs very close together. Also the $4s-4p$ line in S_{IV} does not fit as well as is usual into the irregular doublet law.

The term values were obtained from the lines in the same way as in the case of the two-electron system presented in a preceding paper.

TABLE V

Screening constants for regular doublets, $3p_2-3p_1$

	Δν	$Z-s$	s_3	s_2	s_1
Na					7.450
Mg				7.130	6.606
Al	112.07	5.674	7.326	6.549	6.180
Si	287.	7.177	6.823	6.231	5.916
P	559.5	8.481	6.519	6.042	5.741
S	950.2	9.682	6.318	5.894	5.596
Cl	1500.2	10.853	6.147	5.770	5.504

Table V shows not only how well the relativity or regular doublet law works for triplets, but also how consistent and rational are the values it yields for the screening constant s (columns 4 to 6). Column 6 gives the values of s for one-electron systems (stripped atom doublets), column 5 for two-electron systems (triplets), and column 4 for three-electron systems (doublets). It will be seen that when a particular element is under consideration s for a two-electron system always comes out, as it should, between its values for a one-electron system and for a three-electron system.

TABLE VI

Comparison of term values

	$N=$	3	4	5
	$R/N^2=$	12192.78	6858.44	4389.40
S	Al/1		22933.27	10591.58
	Si/4		16580.8	8462.9
	P/9		13944.2	7477.0
	S/16		12506.8	6908.2
p_1	Al/1	48168.87	15316.48	8003.24
	Si/4	32882.8	12643.0	
	P/9	26974.7	11313.5	
	S/16	23787.0	10489.0	
d_1	Al/1	15844.15	9347.22	6043.31
	Si/4	13119.5	7700.0	
	P/9	14050.0	7878.3	
	S/16	14337.5	7884.5	
f	Al/1		6962.6	4451.5
x	Si/4	19124.5		
	P/9	15903.9		
	S/16	16127.3		

In Table VI are collected in the most convenient form for comparison all of the data now available on the term-values of three-valence-electron atoms. For this comparison, as is indicated in the table, the term-values are divided by 1, 4, 9, 16 in going from Al to S. In this table the silicon term-values have been obtained from Fowler's $3p$ term and from Sawyer and Paton's measured lines above 2000 A. In the case of P_{III} the lines above 2000 A necessary for our computations were taken from Geuter's work.[3]

Table VI shows greater irregularity than the corresponding table for two-valence-electron systems, and this in turn greater irregularity than the corresponding table for stripped atoms. It is not surprising that the

[3] Kayser, Spektroskopie, vol. VI, 246.

irregularities increase with increasing remove from the simple nucleus-electron system. At present we are not able to explain, however, why the d and x terms in the table all pass through a minimum in going from Al to S.

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February 5, 1925

ABSORPTION AND EMISSION SPECTRA OF THE GEISSLER DISCHARGE IN MERCURY VAPOR AND IN MIXTURES OF MERCURY AND HYDROGEN

By Louis A. Turner* and K. T. Compton

Abstract

In a quartz tube 4 cm in diameter, mercury vapor was maintained at about 3 cm pressure and a current of .5 amp. was sent from a tungsten filament cathode to a nickel anode 18 cm away. The absorption of light from a quartz Hg arc lamp on passing transversely through the discharge tube was determined with a small Hilger quartz spectrograph. (1) *Absorption by the continuous positive column.* Several lines of the diffuse and subordinate triplet series were absorbed by atoms in the $2p$ states, $2p-2s$ lines very strongly, $2p-3s$ lines less strongly, $2p-3d$ lines strongly, $2p-4d$ lines less strongly, $2p-5d$ lines weakly. No trace of absorption of combination lines by $2p$ atoms or of absorption by other excited atoms was observed. An unidentified faint line 4279 showed absorption. These results confirm and extend those reported by Metcalfe and Venkatesachar. The absorption by atoms in the $2p_1$ state is greatest but of the same order of magnitude as that by atoms in the $2p_2$ and $2p_3$ states. This is hard to reconcile with the extremely short life of the $2p_2$ state. (2) *Absorption by the striated positive column,* obtained by adding hydrogen. The bright region of the striation showed greater absorption of the $2p-2s$ lines than did the dark regions. (3) *Emission spectra of various parts of the discharge.* The negative glow emitted the arc spectrum and the spark line 2848. All these lines appeared with diminishing intensity through the Faraday dark space. The continuous positive column emitted the arc spectrum. The striated positive column emitted the arc spectrum and HgH bands. The intensity of emission attained its maximum for different lines at different regions in the striations in a manner apparently connected with the excitation energies for the lines.

IN connection with a study of the glow discharge in Hg vapor, the results of which have already been published,[1] many observations of the emission and absorption spectra under different conditions were made. A few of these gave results which had a bearing on the theory of the discharge and were discussed in that connection, but other interesting results were obtained which have not been reported. It seemed advisable to collect all these spectroscopic observations and publish them together.

The apparatus used for the greater part of this work was a tube made of fused quartz, 4 cm in diameter. The electrodes were sealed in through glass tubes attached to the quartz by graded seals. The cathode was a tungsten filament and the anode was a nickel plate placed 18 cm from

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[1] K. T. Compton, Louis A. Turner, and W. G. McCurdy, Phys. Rev. **24**, 597 (1924)

the cathode. A pressure of about 0.3 cm of Hg was maintained in the tube by means of two side arms which contained Hg and were immersed in boiling water. One of these was attached to the closed end of the tube and the other to the outlet connection to the pump. The tube and connections between the two Hg cells were kept at a temperature of 160° by a furnace. Some observations were made visually with a Hilger constant deviation spectroscope. The photographs were made with a small Hilger quartz spectrograph. The source of light for the absorption experiments was a small quartz Hg arc lamp cooled by being half immersed in a pail of running water.

McCurdy[2] found that the presence of a slight amount of impurity was necessary to obtain the striated discharge. He used hydrogen for that purpose and we did the same. By visual observation we found that the light of the three lines of the sharp subordinate series of wave-lengths 5461, 4358, and 4047 was more strongly absorbed in the bright parts of the striations than in the dark spaces between them. This indicates a higher concentration of excited atoms in the $2p$ states in the bright parts of the striations, excited atoms in these states being the absorbers for these lines. The significance of these observations has been discussed fully elsewhere.[1]

When the impurities were pumped out the positive column became uniform and the current through the tube increased greatly. We found by photography that this positive column was a strong absorber for many lines of the sharp and diffuse subordinate series. Inasmuch as the glow itself emitted the whole arc spectrum it was necessary to have a source which would give light of much greater intensity than that emitted by the glow in order to observe the absorption. The cooled mercury arc, with its light concentrated by a suitable lens arrangement, fulfilled this requirement. The exposures were taken in sets of three. The first was a superposition of successive exposures (1a) to the light of the arc alone passing through the tube when the glow was not running and (1b) to the glow alone, both for the same length of time. The second was an exposure to the light of the arc while the glow was running for this same length of time, and the third was taken with the glow alone, also for the same length of time. The absorption of light of any wave-length manifested itself as a diminution in the density of the line in question in the second spectrum as compared with that line in the first spectrum. The third spectrum of the glow alone enabled us to make an estimate of the relative intensity of the total light coming to the spectro-

[2] W. G. McCurdy, Phil. Mag. **48**, 898 (1924)

graph to that from the glow alone. Plate I.A shows several such sets of exposures with time of exposure increasing from top to bottom. Weak absorption is apparent only in the exposures where the line concerned is very weak so that probably the reproduction will show the absorption only for the first lines of the series, for which it is the greatest.

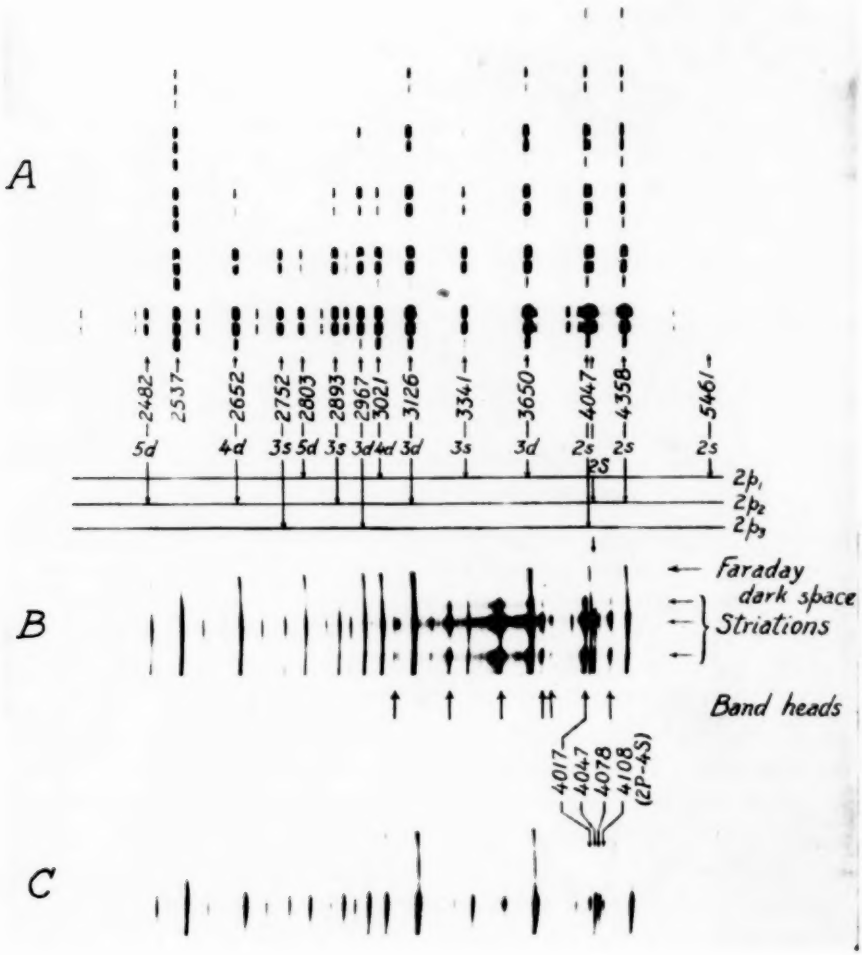

Plate I.

A. Sets of exposures with increasing time, showing absorption by the positive column.
B. Spectrogram showing relative intensities in various parts of positive column.
D. Spectrogram showing variation in length of different lines in a striation.

Table I gives a list of the lines which were absorbed and an estimate of the degree of the absorption of each. Lines which are close together and which were not resolved by the small spectrograph are bracketed together.

TABLE I

Wave-length	Series	Absorption
3663	$2p_1-3d_3$	strong
3655	$2p_1-3d_2$	"
3650	$2p_1-3d_1$	"
3132	$2p_2-3d_3$	"
3126	$2p_2-3d_2$	"
2967	$2p_3-3d_3$	"
3025, 3023, 3021	$2p_1-4d_{3,2,1}$	"
2654, 2652	$2p_2-4d_{3,2}$	medium
2535	$2p_3-4d_3$	?*
2805, 2804, 2803	$2p_1-5d_{3,2,1}$	weak
2483, 2482	$2p_2-5d_{3,2}$	"
5461	$2p_1-2s$	very strong
4358	$2p_2-2s$	strong
4047	$2p_3-2s$	"
3341	$2p_1-3s$	medium
2893	$2p_2-3s$	very slight
2752	$2p_3-3s$	" "

* Too close to 2537 to observe

It will be observed that all of these lines are ones absorbed by atoms in the $2p_{1,2,3}$ states. No absorption of any lines by atoms in the $2P$ or any other state was observed. This is not surprising, for the number of atoms in the $2p$ states was undoubtedly much greater than the number in any other excited state, since an electron which has fallen through a potential drop sufficient to excite a $2p$ state would, in the conditions of our experiments, make an average of more than 1000 collisions before it would acquire sufficient additional energy to excite the $2P$ state. The chance of exciting this state in any other manner than by further excitation of an atom already in the $2p$ state, is therefore negligible. There was no trace of absorption of the combination lines $2p_2-2S$ and $2p_2-3S$ of wave-lengths 4078 and 2857. The combination lines of the $2p-mD$

series are too close to the $2p-md_3$ lines to be separated. In addition, an unidentified faint line of approximate wave-length 4279 showed some absorption.

These results are a slight extension of those obtained by Metcalfe and Venkatesachar[3] with a somewhat different apparatus. They used an arc between two pools of Hg and observed the absorption in a column of glowing vapor 52 cm long, excited by a subsidiary anode. Apparently our arrangement is more efficient in producing excited atoms for we observed greater absorption of light passing transversely through our tube 4 cm in diameter than they did with their long tube, the current density in our tube being 40 milliamp. per cm^2 as compared with 10 milliamp. per cm^2 in their experiment. One would expect the concentration of excited atoms to be proportional to the current density, other things being equal. Differences in vapor pressure of the Hg may account for the different results. The value of the pressure in their experiment is uncertain but was presumably less than in ours. Of the above lines they observed absorption of only the $2p_{1,2,3}-3d$, the $2p_{1,2,3}-2s$, and the $2p_1-3s$ lines. Our plates do not show the lines 5289, 5295, and 5308 which they found to be slightly absorbed.

The relative intensities of absorption by the atoms in the $2p_1$, $2p_2$, and $2p_3$ states is a matter of interest. The fact that the absorption by these three varieties of excited atoms is of the same order of magnitude is hard to account for. The p_1 and p_3 atoms are metastable and of relatively long life,[4] so that it is easy to see how a considerable concentration of them could be built up, but several independent methods[5] of estimating the life of the atom in the $2p_2$ state agree that it is approximately 10^{-7} second, so that considerable concentrations of atoms in that state would be attained only by high rates of excitation. Zernicke[6] observed that vapor diffusing from the discharge into a space shielded electrically from it, showed absorption by the $2p_1$ and $2p_3$ atoms but not by the $2p_2$ atoms. Our result indicates that either the atomic absorption coefficients for the $2p_2$ atoms is very great or that the rate of production of such excited atoms is much greater than that for the other two varieties. Perhaps there is some sort of an equilibrium established among the three states

[3] Metcalfe and Venkatesachar, Proc. Roy. Soc. A **100,** 149 (1921)

[4] Milton Marshall, Astrophys. Jour. **60,** 243 (1924)

[5] W. Wien, Ann. der Phys. **73,** 483 (1924);
Richard C. Tolman, Phys. Rev. **23,** 693 (1924);
Louis A. Turner, Phys. Rev. **23,** 464 (1924);
John A. Eldridge, Phys. Rev. **24,** 234 (1924).

[6] K. T. Compton and F. L. Mohler, Bull. Nat. Res. Coun. **9,** No. 48, p. 91.

by collisions of the first and second kind. Undoubtedly, the "imprisonment"[7] of the 2537 resonance radiation plays a part by increasing the length of time that the excitation energy remains in the vapor, an effect equivalent to a longer life of the atom in the $2p_2$ state. We observed a somewhat greater absorption of lines by the atoms in the $2p_1$ state than of the corresponding lines for the $2p_2$ or $2p_3$ states. Whether this depends upon a greater concentration of atoms in the $2p_1$ state or upon a greater atomic absorption coefficient cannot be said. It is of interest in this connection to note that Marshall[4] found that the life of the $2p_1$ excited atoms was eight times that of the $2p_3$ excited atoms. We hope that the future may offer the opportunity to make an accurate quantitative investigation of this absorption.

Photographs of the emission spectrum from the tube were taken by focusing an image of the tube on the slit of the spectrograph with the axis of the tube parallel to the slit, the striations being perpendicular to it. The negative glow shows, in emission, all the lines of the arc spectrum, the prominent spark line of wave-length 2848, and the strong raies ultimes of the W spectrum of wave-lengths 4295 and 4009. These lines are emitted with diminishing intensity through the Faraday dark space, showing no discontinuity until the edge of the continuous positive column or of the first striation, as the case may be, is reached. The first striation is usually closer to the second than the fairly uniform spacing of the others and appears to the eye to be less intense than any of the others. The second one appears to be the most intense. These differences show themselves with the spectrograph, the intensity changes apparently being the same for all the lines of the arc spectrum. The continuous positive column shows simply a uniform emission of the lines of the arc spectrum throughout its length. When there is much hydrogen present in the tube the HgH bands[8] appear with considerable intensity in the positive column, but not in the other regions of the discharge. They are of more nearly uniform intensity in all the striations than are the lines (Plate IB). Their intensity is roughly proportional to the amount of hydrogen present.

Different lines appear to be of different length, in the second striation in particular. That is, it appears as if the maximum intensity of emission of the different lines occurred in different parts of the striation. This is particularly noticeable in the group of three lines of wave-lengths 4047, 4078, and 4108 (Plate IC). It so happens that the order of

[7] K. T. Compton, Phil. Mag. **45**, 450 (1923)

[8] K. T. Compton and Louis A. Turner, Phil. Mag. **48**, 360 (1924)

length of these three lines is the same as the order of intensity. One set of exposures of different lengths of time taken from the same striations shows that it is not an intensity effect, however, for the apparent lengths of the lines stay the same in all the exposures even though the stronger one in a short exposure is of about the same density as the weaker one in a long exposure. It also happens that the lengths are in inverse order to the excitation energies of the upper stationary states involved in their emission and the differences in length are roughly proportional to the differences between the energies of these upper states. The ultraviolet lines were not in good enough focus on the slit to enable us to extend these observations to them. A refined investigation of this effect, might, however, give valuable information concerning the mechanism of the discharge in the striated positive column.

These experiments were performed in the Palmer Physical Laboratory of Princeton University.

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February 2, 1925

ABSORPTION OF A LINE OF THE PRINCIPAL SERIES OF SINGLY IONIZED ATOMIC MERCURY

By Louis A. Turner* and K. T. Compton

Abstract

Evidence as to series relations of the mercury lines 1942, 2225 and 2848.—Light from an electrodeless discharge in Hg vapor was passed through a region of a low voltage arc in Hg vapor containing a high concentration of positive ions. The 1942 spark line showed *absorption*; the 2225 and 2848 spark lines did not show absorption. A rough determination of the *excitation potentials* showed these to be much higher for the 2225 and 2848 lines than for the 1942 line. These experiments verify J. A. Carroll's conclusion that the 1942 line is a member of the principal series, and that the other two are members of subordinate series of Hg.

THE Kossel-Sommerfeld[1] displacement law states that the first spark spectrum of any element is similar in structure to the arc spectrum of the element whose atomic number is less by one. Thus the spark spectra of the alkaline-earth metals are systems of doublets like those of the arc spectra of the alkali metals. This is also true of the spark spectra of Zn and Cd and consequently would be expected to be true of the spark spectrum of Hg which has an arc spectrum of structure very similar to that of the arc spectra of all of these elements. This expectation has recently been augmented by Thorsen's[2] arrangement of the lines of the arc spectrum of Au, the element next below Hg in the periodic table. He found a doublet system in this spectrum. Rydberg[3] suggested that perhaps the two prominent spark lines of Hg of wave-lengths 2225 and 2848 were the first pair of the principal series.

If this surmise were correct, light of these wave-lengths should be strongly absorbed in passing through a region where there is a sufficient concentration of singly charged Hg ions, i.e. a sufficient partial pressure of what is from this point of view a new substance, Hg^+. If these lines are really the first members of the principal series, light of these wave-lengths should be absorbed by positive ions in the normal state, which are atoms with one valence electron completely removed but with all the others in their normal orbits. Such is the explanation for the ap-

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[1] A. Sommerfeld, "Atombau und Spectrallinien," 3rd Ed., p. 457.

[2] Thorsen, Die Naturwissenschaften, 11, p. 500, 1923.

[3] A. Fowler, "Report on Series in Line Spectra," p. 151.

pearance of the first principal pair of the spark spectrum of Ca as the strong H and K Fraunhofer lines. Foote and Mohler[4] state, however, that hitherto no laboratory experiments of this sort have been performed.

The measurements[5] of the concentrations of positive ions in discharges in Hg vapor showed a high concentration in the neighborhood of the hot filament cathode and suggested to us that such a region might contain a sufficient concentration of these ions to show this absorption. Accordingly, we undertook experiments to test the matter.

While this work was in progress we heard of a new arrangement of the Hg^+ spectrum by J. A. Carroll, as yet unpublished. We are greatly indebted to him for his kind permission to refer to his results in this article. According to Carroll the first pair of the principal series consists of the lines of wave-lengths 1649.8 and 1942.5. The wave-length of the first of these is too short for us to observe it with our spectroscopic equipment, but we were able to photograph the latter with a small quartz spectrograph. We found no indications of an absorption of the lines 2225 and 2848 but found a decided absorption of 1942, thus verifying Carroll's arrangement.

Apparatus and Results

For the experiment we needed an intense source of ultraviolet light and an absorbing tube which would give a maximum concentration of positive ions in the normal state with a minimum amount of emission of the spark lines. We adopted, for the source, an electrodeless ring discharge in Hg vapor contained in a small fused quartz bulb. It could be adjusted, by regulation of the vapor pressure of Hg, to give radiation of great intensity in the spark lines in which we were particularly interested. For the absorber we used a low-voltage arc discharge in Hg vapor from which the emission of the spark lines was weak. In such a discharge ionization is presumably produced by cumulative[6] effects so that there are very few electrons present having sufficient velocity to excite the spark lines. Fig. 1 is a diagram of the apparatus. The cathode was a fifteen mil (.4 mm) tungsten filament. The anode was a liquid Hg surface of adjustable height. A double set of windows made of fluorite plates was used. The inner ones were within the furnace and at the temperature of the liquid Hg so that no condensation on them occurred. They were pressed against the flat ground ends of the projecting side

[4] Foote and Mohler, "The Origin of Spectra," p. 103.
[5] W. G. McCurdy, Phil. Mag. **48**, 898 (1924)
[6] K. T. Compton, Phys. Rev. **20**, 283 (1922). See also Foote and Mohler, "Origin of Spectra," p. 154.

tubes and made contact sufficiently well so that practically no Hg vapor leaked out and there was no difficulty from condensation of Hg on the outer, cold, windows which were sealed on with deKhotinsky cement. The spectrograph was a small Hilger quartz instrument, of size A. We used Seed 60 plates sensitized for the short wave-lengths with Nujol.[7] The method of exposure was first to superimpose separate exposures of the same length of time (1) from the source without the discharge in the absorbing tube running, and (2) from the discharge in the absorbing tube alone, by exposing them successively. This was followed by another exposure of the same length of time taken with the two running simultaneously so that the light from the source passed through the region of the discharge in the absorbing tube. Any absorption of the light from the source showed itself as a diminution in the density of the line in the second spectrum as compared with the same line in the first spectrum.

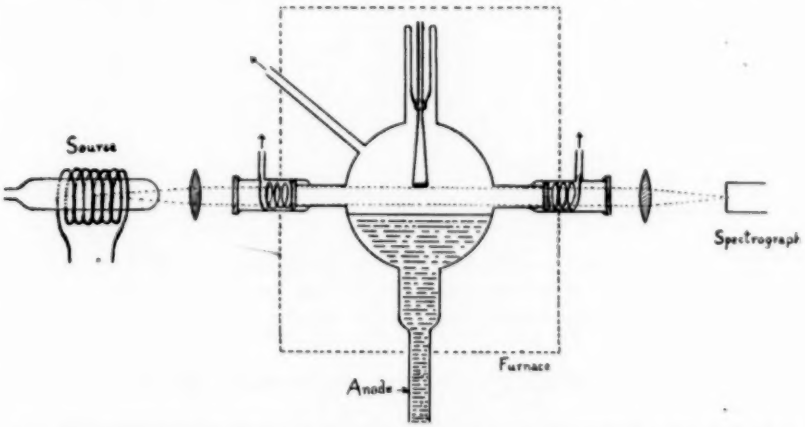

Fig. 1. Apparatus showing electrodeless source, and absorption tube in furnace.

The best results were obtained with the temperature of the absorbing tube at 135° (giving a vapor pressure of Hg of 1 mm), an applied arc voltage of 6.6 volts and an arc current of 2 amp. On the basis of other measurements in similar discharge tubes, the partial pressure of positive ions is estimated to be about 5 $(10)^{-5}$ mm of Hg. The effective length of the absorbing path was about 5 cm. The plates showed a distinct weakening of the 1942 line but no weakening of the 2225 and 2848 lines. Measurements made at Harvard with Dr. George R. Harrison's densitometer showed a marked decrease in the intensity of the 1942 line but only small variations in the densities of other spark lines of comparable intensity

[7] Ducleaux et Jeantet, Jour. de Physique **11**, 154 (1921); T. Lyman, Science, p. 48, July 20, 1921.

chosen at random. We estimate that about one fourth of the incident light was absorbed, but because of lack of sufficient data for the establishment of the characteristic curve of the photographic plate at this wavelength, this estimate may be in error by a factor of 2 one way or the other.

Fig. 2 shows a set of densitometer curves for line 1942 from one set of exposures. The original photographs of the spectra are similar to those shown in Fig. 1 of the preceding paper, and are not reproduced here.

Measurements made with other lines showed an increasing intensity from (1) to (6).

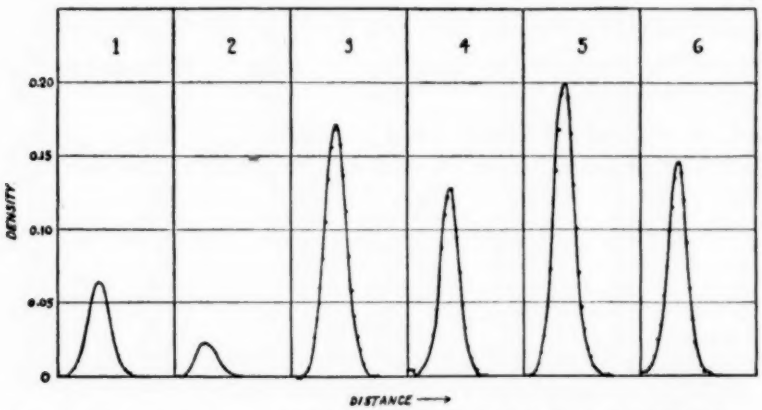

Fig. 2. Densitometer curves for line 1942. 1. Source alone. 2. Absorber alone. 3 and 5. Superposition of exposures from source and absorber. 4 and 6. Light from source through absorber.

Excitation Energies of Spark Lines

We took a set of exposures of the light emitted from the discharge tube for different anode voltages, the current through the tube being kept the same for all by regulation of the filament current. The anode voltages for these exposures were 4.5, 5.3, 6.7, 8.1, 9.4, 10.7, 12.3, 14.5, . . . The 1942 line appeared first at 6.7 volts, the 2848 line at 10.7 volts, and the 2225 line at 12.3 volts. The relative intensities after the appearance of all the lines showed that these differences were not merely the result of intensity differences. This would seem to indicate that the two lines of the Rydberg "doublet" belong to subordinate series, which is in accord with Carroll's conclusions.

As the anode voltage was lowered and the filament current was increased to keep the current in the tube constant, a condition was reached such that further reductions in the voltage could only be secured by very great increases of the filament current, the voltage dropping suddenly.

The spectrum of the light emitted after this voltage drop was very much more intense, even though the current density was the same. The spark lines were present with considerable intensity. Apparently this was the condition for the oscillating discharge[8] so that electrons of high velocity were present in the tube for a part of the time.

In conclusion we wish to thank Dr. Harrison for the use of his densitometer. These experiments were carried out in the Palmer Physical Laboratory of Princeton University.

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February 2, 1925

[8] Carl Eckart and K. T. Compton, Phys. Rev. 24, 97 (1924)

THE DENSITY OF ROCK SALT AND CALCITE

By O. K. DeFoe and Arthur H. Compton

Abstract

Crystals as perfect as could be secured were obtained from a variety of sources, and densities were measured by weighing them when suspended in paraffine oil or water respectively. The weights were calibrated and correction was made for the buoyancy of the air. The measurements are accurate to .2 mg cm^{-3} for rock salt and to .1 mg cm^{-3} for calcite. Variations in density were observed between different parts of the same crystal, as well as between different crystals, which are larger than the experimental error. The estimated uncertainty of the mean density is taken as the probable variation of the individual samples from the mean density. The mean result for 7 good crystals of rock salt is $2.1632 \pm .0004$ gm cm^{-3}, and for 6 crystals of calcite, $2.7102 \pm .0004$ gm cm^{-3}, at 20°C.

IN order to increase the precision of absolute x-ray wave-lengths, we have undertaken the redetermination of the densities of rock salt and calcite. For this purpose we have secured samples as perfect as we could obtain, from a variety of different sources. Some of these were loaned to us by the National Museum at Washington, to whom we wish to express our grateful acknowledgment.

Our experimental method was in its essentials that described by D. C. Miller.[1] The weights used were carefully calibrated, and the weighings were corrected for the buoyancy of the air. The density of calcite was determined by suspension in freshly boiled distilled water, whose density was used as the standard. For rock salt, paraffine oil was used in order not to dissolve the crystal. The density of the oil was compared with that of water through the medium of a plumb bob, which consisted in one set of measurements of fused quartz, in another of Pyrex glass and in a third of a calcite crystal. Because of the comparatively large thermal expansion coefficient of the oil, the density determinations for rock salt were not as precise as those for calcite.

The results of the measurements on nearly perfect crystals are given in the following table. We have not counted measurements on crystals in which serious imperfections were observed. In reducing the results to 0°C, we have taken Benoit's values for the thermal expansion coefficient of calcite[2] as $+0.0000251$ deg.$^{-1}$ parallel with the crystal axis and -0.0000056 deg.$^{-1}$ perpendicular to the axis. It follows that $\rho_0 =$

[1] D. C. Miller, "Laboratory Physics" (1903) pp. 120-123.

[2] Cf Kaye and Laby, "Physical and Chemical Constants" (1911) p. 53.

$\rho(1+.0000139t)$ where t is the centigrade temperature. Similarly for rock salt,[3] $\rho_0=\rho(1+.0001212\,t)$. The average temperature at which the measurements were made was about 23°.

TABLE I

Densities of rock salt and calcite
I and II refer to two parts of the same crystal.

Rock salt		Calcite	
Origin	Density (0°C)	Origin	Density (0°C)
Michigan I	2.1687	Missouri	2.7114
Michigan II	2.1683	U. S. A.	2.7110
Arizona I	2.1687	Iceland	2.7111
Arizona II	2.1683	Iceland	2.7098*
Germany I	2.1687	Unknown	2.7109
Germany II	2.1676*	Unknown	2.7112
Unknown	2.1687		
Mean	2.1685	Mean	2.7110

* Weighted 1/2 in calculating mean.

In the case of calcite the determinations of the density of the individual samples were made within a probable error of $\pm.0001$ gm cm^{-3}, and for rock salt within $\pm.0002$ gm cm^{-3}. The experiments thus indicate that different samples of apparently perfect crystals vary in density by amounts greater than the experimental error of our measurements. No chemical analysis was attempted to search for possible impurities which might account for these variations. One of the samples of rock salt (Michigan I) was however tested by Mr. C. C. Van Voorhis for occluded water, by melting in an evacuated Pyrex tube and drawing the liberated gases over phosphorous pentoxide. A similar test with no salt present showed that, if any moisture was occluded in the rock salt, it was an amount small compared with that which escaped from the Pyrex container, even though this had previously been baked out at a high temperature.

In view of these variations in density from one part of an apparently perfect crystal to another, we are unable to determine which value represents the true density of a perfect crystal. As an estimate of the probable error in the value of the density we are therefore on safer ground if we choose the probable variation of the density of any individual crystal from the mean value for all crystals. Thus we determine the following densities:

Calcite: $\rho=2.7110\pm.0004$ gm cm^{-3} at 0° C.
$=2.7102\pm.0004$ gm cm^{-3} at 20° C.

[3] Cf Landolt, Bornstein, Roth, "Tabellen" (1912), p. 336.

Rock salt: $\rho = 2.1685 \pm .0004$ gm cm^{-3} at 0°C.
$= 2.1632 \pm .0004$ gm cm^{-3} at 20°C.

These values are compared with those given by other authorities, in Table II.

TABLE II

Values for the density of calcite and rock salt

	Authority	Date	Density
Calcite	Clarke[4]	1873	2.723
	Schroeder[5]	1874	2.702
	Retgers[6]	1890	2.712
	Dana[7]	1892	$2.65 \pm .05$
	Bragg[8]	1915	2.71
	Compton[9]	1916	$2.7116 \pm .0004$ (at 18°)
	Ledeaux, Lebard and Dauvillier[10]	1919	$2.7125 \pm .0015$
	This determination	1925	$2.7102 \pm .0004$ (at 20°)
Rock salt	Clarke[9]	1873	2.135
	Retgers[11]	1889	2.167 (at 17°)
	Dana[7a]	1892	$2.15 \pm .05$
	Krickmeyer[12]	1896	2.174 (at 20°)
	Haigh[13]	1912	2.170 (at 20°)
	Moseley[14]	1913	2.167
	Baxter and Wallace[15]	1916	2.161
	This determination	1925	$2.1632 \pm .0004$ (at 20°)

A calculation of the grating spaces of rock salt and calcite based on this determination of their densities is described elsewhere in this journal.[16]

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[4] Clarke, "Constants of Nature" (1873) v. 1, p. 30.
[5] Schroeder, "Neue Handbuch f. Minerologie" (1874) p. 805.
[6] Retgers, Zeits. Phys. Chem. **6**, 193 (1890).
[7] Dana, "System of Minerology" (1892).
[8] W. H. Bragg and W. L. Bragg, "X-rays and Crystal Structure" (1915) p. 115.
[9] A. H. Compton, Phys. Rev. **7**, 646 (1916). In this measurement no correction was made for the buoyancy of the air. Such a correction makes this value agree well with the present determination.
[10] Ledeaux, Lebard and Dauvillier, Compt. Rend. Nov. 24, 1919. This value is based chiefly on that by A. H. Compton,[9] and is hence also subject to a correction for the buoyancy of the air.
[11] Retgers, Zeits. Phys. Chem. **3**, 289 (1889)
[12] Krickmeyer, Zeits. Phys. Chem., **21**, 53 (1896).
[13] Haigh, J. Am. Chem. Soc. **34**, 1137 (1912)
[14] H. G. J. Moseley, Phil. Mag. **26**, 1024 (1913).
[15] Baxter and Wallace, J. Am. Chem. Soc. **38**, 26 (1916).
[16] A. H. Compton, H. N. Beets and O. K. DeFoe, in this issue, p. 625.

A DETERMINATION OF THE ANGLE BETWEEN THE CLEAVAGE FACES OF CALCITE BY USE OF X-RAYS

By Henry Nicholas Beets*

Abstract

The dihedral angle was determined by measuring the angle through which the crystal must be turned to reflect the MoKα line, first from one cleavage face and then from the adjacent face. Of the six crystals studied, one gave imperfectly cleaved surfaces, one showed slightly rippled faces, the others gave for the mean dihedral angle 74° 55′.0±.2′ in excellent agreement with optical determinations. This corresponds to an angle between the edges of the crystal of $\beta = 101°\ 55.0 \pm .2'$. From the coefficients of thermal expansion the change of β with temperature is $d\beta/dt = -.051'$ per degree. The volume of a rhombohedron the distance between whose opposite faces is unity comes out 1.09630±.00007 at 20°C.

THE present investigation has for its object a measurement of the angles between the faces of calcite, which has been considered[1] one of the important sources of error in the determination of its grating space. The grating space of calcite can be calculated from the relation[2]

$$D = [\tfrac{1}{2} M/\rho N \varphi(\beta)]^{1/3} \tag{1}$$

where M is the molecular weight of calcite, ρ is its density, N is the number of molecules per mol, and $\varphi(\beta)$ is the volume of a rhombohedron the distance between whose opposite faces is unity and the angle between whose edges is β. From spherical trigonometry,

$$\varphi(\beta) = \frac{(1+\cos\beta)^2}{(1+2\cos\beta)\sin\beta}, \tag{2}$$

where

$$\cos\tfrac{1}{2}\beta = 1/(2\sin\tfrac{1}{2}\alpha), \tag{3}$$

and α is the interior obtuse dihedral angle of the crystal.

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[1] H. S. Uhler, Phys. Rev. **12**, 39 (1918).

[2] W. H. Bragg, Proc. Roy. Soc. A **89**, 468 (1914).

The following values of $180° - \alpha$ are given by crystallographers from goniometric measurements

$180° - \alpha$	Temperature	Observer
74° 56′.°	ordinary	Groth[3]
74 55.5	10°C	Mitscherlich[4]
74 54.93	20	Hastings[5] (calculated)
74 55.5	ordinary	Kuppfer[6]
74 54.25	"	Breithaupt[6]
74 55	"	Breithaupt[6]
74 55.2	"	Roth[6]
74 56	"	Koksharov[6]
74 55	"	Dana[6]
74 55	"	Zolton Toborffy[7]
74 55	"	Zolton Toborffy[7]
74 55	"	Malus[8]

The mean of these values, assigning equal weights to each, is 74° 55′.2, with a probable difference from the mean for each determination of ±.3′.

It was suggested by A. H. Compton that the angle be measured in a new way which might well be called the x-ray goniometric method, namely, that x-rays of a given wave-length be reflected from one cleavage face of the crystal and the crystal then be revolved till reflection of the same wave-length and order be obtained from the adjacent cleavage face. The angle through which the crystal is turned is then either the desired angle or its supplement.

Method and Apparatus

The method employed is similar to Bragg's third method of crystal analysis.[9] The crystal is made to revolve while the ionization chamber stands still, its slit being wide open. The incident pencil of x-rays is made as fine as possible, one of the limiting slits being placed as close to the crystal as is conveniently possible.

The crystal is mounted on the spectrometer table by means of a holder which can be moved in accurately parallel grooves so that the crystal faces can be moved parallel to themselves without changing the angle made by the beam with the crystal face. The table is so placed that the x-ray beam passes through the prolongation of the axis of the table. The ionization chamber is placed at the calculated angle for the reflection of the wave-length used, in this case the Kα line of molybdenum. The width of the chamber slit permits some latitude in the position of the chamber.

[3] Groth, "Physikallische Kristallographie," (1905).
[4] Metscherlich, cf Liebisch, "Physikallische Kristallographie" (1891).
[5] Hastings, Am. Jour. Sci. **35,** 68 (1888).
[6] Quoted by Dana, "System of Mineralogy."
[7] Zolton Toborffij, Zeits. f. Kristallographie **44,** 605 (1908).
[8] H. Buttgenbach, "Constantes Geometrique des Mineraux," (1918).
[9] Bragg, "X-Rays and Crystal Structure," 3d ed., p. 29.

The crystal is so mounted that its edge is parallel to the axis of rotation of the table and about 2 mm to one side of it, the prolongation of the axis lying in the face of the crystal. The crystal is gradually turned till the Kα line is reflected into the ionization chamber. It was not found possible under the conditions of the experiment to resolve the $K\alpha_1$ and the $K\alpha_2$ lines, but fairly sharp peaks were obtained. The setting of the crystal at the peak is noted, and the crystal then rotated to the second position, that is, for reflection from the second face, the crystal being moved backward or forward parallel to itself if necessary.

In this investigation the distance between the slits collimating the primary beam was 15 cm, and their width 0.08 mm. The x-ray source was a molybdenum target Coolidge tube operated at 40 kv and 12 milliamp. The ionization chamber was filled with sulphur dioxide. A Compton quadrant electrometer with a sensitivity of 2000 mm per volt indicated the ionization current. The circle of the Geneva spectrometer could be read to seconds of arc with the aid of the reading microscopes.

Six crystals of varying size, each having fairly good cleavage faces, were measured. The angles obtained were corrected for any errors in the centering of the table by reading both sides of the table and taking the mean. The average temperature at which the readings were taken was 22°C. The values obtained are given in the following table.

Crystal	Size and description	Angle	Weight
1	2×2×1.5 cm. Faces slightly rippled; white cloudy inclusion	74°56.0′	0
2	1.5×3.5×1.5 cm. Faces good	105 5.2	2
		105 5.2	2
		74 55.0	2
		74 55.0	2
3	3×5×3 cm. Large crystal, faces not perfectly cleaved	74 57.5	0
4	1×3×4 cm. Faces free from ripples	74 55.5	2
		74 55.5	2
5	0.3×2.2×0.3 cm. Perfect faces.	74 54.9	3
		74 54.9	3
6	1×3×3 cm. One cleavage face, one polished face	74 55.0	2
		74 54.8	2
		74 54.8	2
		74 55.0	2

These give a most probable angle* of 74° 55′.0±.2′. It will be seen that this value is in excellent agreement with that obtained by the usual

* The greater part of the variations in the readings seem to be due to accidental differences between the different crystals rather than to experimental errors. The probable error here used (±.2′) is therefore the probable difference of any one of the good crystals from the mean value.

goniometric methods. The angle α is the supplement and is $105° 5'.0 \pm .2'$. From this angle β is calculated to be $101° 55'.0 \pm .2'$, and $\varphi(\beta)$ is 1.09627 $\pm .00007$ at 22°.

In view of the fact that the thermal expansion coefficient of calcite differs in different directions, the angle β will vary somewhat with the temperature. If k_p and k_s are respectively the expansion coefficients parallel and perpendicular to the crystal axis, it can be shown that the change of the angle β with the temperature is,

$$d\beta/dt = 2 \tan \tfrac{1}{2}\beta(1 - \tfrac{3}{4}\sin^2 \tfrac{1}{2}\beta)(k_s - k_p). \qquad (4)$$

Using Benoit's values[10], $k_p = .0000251$ deg.$^{-1}$, and $k_s = -.0000056$ deg.$^{-1}$, this gives an angular change of $d\beta/dt = -0.051'$ per centigrade degree. Similarly $\varphi(\beta)$ diminishes with increasing temperature by 0.000018 per degree. At 20°C we thus have,

$$\beta = 101° 55'.1 \pm .2'$$

$$180° - \alpha = 74° 49'.9 \pm .2'$$

and

$$\varphi(\beta) = 1.09630 \pm .00007.$$

The present value of $\varphi(\beta)$ is to be compared with the value 1.09626 $\pm .0007$ estimated by Uhler[1] in 1918 on the basis of data which he collected.

While more precise measurements of β would doubtless be possible by this method, the present determination has reduced the probable error in the grating space from this source to a value which is small compared with that from other sources, thus accomplishing the object of the experiments. The grating space of calcite calculated with the use of this measurement is given elsewhere in this journal.[11]

In conclusion, the writer wishes to thank Professor A. H. Compton for his continued help and valuable suggestions throughout the course of the work.

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[10] Cf Kaye and Laby, "Physical and Chemical Constants" (1911), p. 53.
[11] A. H. Compton, H. N. Beets and O. K. DeFoe, following paper.

THE GRATING SPACE OF CALCITE AND ROCK SALT

By A. H. Compton, H. N. Beets* and O. K. DeFoe

Abstract

Grating spaces of calcite and rock salt are recalculated using the new values for the crystal densities obtained by DeFoe and Compton, and come out for calcite 3.0291±.0010A and for rock salt, 2.8147±.0009A at 20°C. The values for each degree from 15° to 25° are given in a table. These values are slightly greater than those usually given. The remaining uncertainty is due chiefly to that in Avogadro's number. The ratio $D(CaCO_3)/D(NaCl)$ comes out 1.0762 ±.0002(18°C) which agrees satisfactorily with Siegbahn's value, 1.0764. The uncertainty in this value is chiefly associated with the molecular weights.

Absolute wave-length values corrected for refraction.—The correction is made by using an effective grating space slightly smaller than the true value. For the first order from calcite the effective value is 3.0287 and for rock salt 2.8144A, both at 20°C. Using these values the *wave-length of Mo* $K\alpha_1$ line is found (Siegbahn) to be .70749±.00023A.

ACCORDING to Bragg's law the wave-length λ of a beam of x-rays reflected from a crystal at a glancing angle θ is given by

$$n\lambda = 2D\sin\theta, \tag{1}$$

or more precisely by

$$n\lambda = 2D\sin\theta(1-\delta/\sin^2\theta), \tag{2}$$

where n is the order of the spectrum, D is the grating space or distance between successive layers of atoms in the crystal grating, and $\delta = 1-\mu$, μ being the index of refraction of the x-rays in the crystal. At present it is possible to measure θ to a degree of accuracy such that by far the greater part of the error in determining the absolute wave-length of a beam of x-rays is due to the uncertainty of D. It is thus of obvious importance to determine this grating space with precision.

From very fundamental considerations of the principles underlying crystal structure, it can be shown that the grating space of a rhombohedral crystal is given by

$$D = (nM/\rho N\varphi(\beta))^{1/3}, \tag{3}$$

where n is the number of molecules per elementary rhombohedron, M is the molecular weight, ρ the density, N the number of molecules per gram molecule, and $\varphi(\beta)$ is the volume of a rhombohedron the distance

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between whose opposite faces is unity and the angle between whose edges, β, is that between the axes of the crystal. For the two most commonly used crystals, rock salt and calcite, $n=1/2$, and M is known with rather high precision. For rock salt, $\beta=90°$, whence $\varphi(\beta)=1$; but for calcite the uncertainty of the value of β has been considered an appreciable source of error.[1] The density ρ does not appear to have been measured for either crystal with the care its importance would warrant, so that it also contributes appreciably to the probable error. In estimating D, the uncertainty of the value of N introduces the greatest single source of error, though no greater than that which Uhler estimates[1] as due to the combined error of ρ and β in the case of calcite.

By introducing the values of ρ and β which we have measured as described elsewhere in this journal, we are able to reduce somewhat the probable error of the calculation of the grating spaces of calcite and rock salt from Eq. (3). We have:

For calcite,	For rock salt,
$n=1/2$[2]	$n=1/2$[2]
$M=100.075\pm.03$[3]	$M=58.46\pm.02$[3]
$\rho=2.7102\pm.0004$ at 20°[4]	$\rho=2.1632\pm.0004$ at 20°[4]
$N=(6.0594\pm.006)\times10^{23}$[5]	$N=(6.0594\pm.006)\times10^{23}$[5]
$\varphi(\beta)=1.09630\pm.00007$ at 20°[6]	$\varphi(\beta)=1.$

Substituting these values in equation (3) we obtain

$$D(CaCO_3)=(3.0291\pm.0010)\times10^{-8}\text{ cm at }20°\text{ C};$$
$$D(NaCl)=(2.8147\pm.0009)\times10^{-8}\text{ cm at }20°\text{ C}.$$

The thermal expansion coefficient of these crystals, though not large, is sufficient to make corrections necessary for precise measurements. Perpendicular to the cleavage faces, this coefficient is for calcite[7] 0.0000104 and for rock salt[8] 0.0000404 per degree centigrade. If we use the value 3.02910 as the value of the grating space of calcite, and 2.81470 as that of rock salt at 20°C, their values at other temperatures are given in the following table.

[1] H. S. Uhler, Phys. Rev. **12**, 42 (1918).

[2] W. H. Bragg and W. L. Bragg, "X-Rays and Crystal Structure," (1915).

[3] International Atomic Weights, 1921. The estimates of the accuracy are our own, made chiefly on the basis of the data collected by F. W. Clarke, "A Recalculation of Atomic Weights" (1920).

[4] O. K. DeFoe and A. H. Compton in this issue, p. 618.

[5] R. T. Birge, Phys. Rev. **14**, 365 (1919).

[6] H. N. Beets, preceding paper.

[7] M. Siegbahn, "Spektroskopie der Roentgenstrahlen," p. 86 (1924).

[8] Fizeau. Cf Landolt, Bornstein, Roth "Tabellen" p. 336 (1912).

TABLE I

Grating space of calcite and rock salt at different temperatures

T	$D(CaCO_3)$	D(NaCl)
15°C	3.02894	2.81413
16	3.02898	2.81425
17	3.02901	2.81436
18	3.02904	2.81447
19	3.02907	2.81459
20	(3.02910)	(2.81470)
21	3.02913	2.81481
22	3.02916	2.81493
23	3.02919	2.81504
24	3.02923	2.81515
25	3.02926	2.81527

It is interesting to compare these values of the grating spaces with those previously employed.

For calcite

D	Authority	Date
3.04×10^{-8}cm	W. H. Bragg[9]	1914
3.028	W. S. Gorton[10]	1916
3.0279	A. H. Compton[11]	1916
3.0307	Uhler and Cooksey[12]	1917
3.030	Millikan[13]	1917
3.0281	A. H. Compton[14]	1918
$3.0283\pm.0022$ / 3.02904 at 18°	M. Siegbahn[15]	1919
3.028	Duane[16]	1920
3.02855	McKeehan[17]	1922
$3.0291\pm.0010$ at 20°	This determination	1925

For rock salt

D	Authority	Date
2.80×10^{-8}cm	W. L. Bragg[18]	1913
2.814	Moseley[19]	1913
2.814	E. Wagner[20]	1916
2.810	Davey[21]	1921
2.814	Siegbahn[22]	1924
2.815	Davey[23]	1924
$2.8147\pm.0009$ at 20°	This determination	1925

[9] W. H. Bragg, Proc. Roy. Soc. A **89,** 468 (1914).

[10] W. S. Gorton, Phys. Rev. **7,** 209 (1916).

[11] A. H. Compton, Phys. Rev. **7,** 655 (1916).

[12] H. S. Uhler and C. D. Cooksey, Phys. Rev. **10,** 645 (1917); by comparison, assuming D(NaCl) = 2.8140 A.

[13] R. A. Millikan, Phil. Mag. **34,** 13 (1917).

[14] A. H. Compton, Phys. Rev. **11,** 431 (1918).

[15] M. Siegbahn, Phil. Mag. **37,** 601 (1919); 3.02904 obtained by comparison, assuming D(NaCl) at 18° = 2.81400 A.

[16] W. Duane, Bull. Nat. Res. Council No. 7 (1920).

[17] L. W. McKeehan, Science, N. S. **56,** 757 (1922); average by comparison with rock salt.

[18] W. L. Bragg, "X-Rays and Crystal Structure," (1915) p. 110.

[19] H. G. J. Moseley, Phil. Mag. **26,** 1024 (1913).

[20] E. Wagner, Ann. der Phys. **49,** 625 (1916).

[21] W. P. Davey, Science, **54,** 497 (1921).

[22] [23] See footnotes on the next page.

There has heretofore been a discrepancy between the observed and the calculated values of the ratio $D(CaCO_3)/D(NaCl)$, which has seemed larger than the probable error of the determinations.[24] It will be noticed that this ratio does not involve N, which is responsible for the greatest part of the probable error of D. Our calculated value of this ratio is $1.0762 \pm .0002$ at 18°, in which the greatest part of the uncertainty is due to the molecular weights. This is to be compared with Uhler and Cooksey's[12] value 1.07701 and Siegbahn's[15] value 1.076417 at 18°, both of which were determined by direct spectrometric methods. It will be seen that the agreement with Siegbahn's value, which is the more accurate of the two experimental determinations, is almost within the estimated probable error. There thus remains no significant discrepancy between the calculated and the observed ratios of the grating spaces of rock salt and calcite.

In view of the fact that calcite crystals are much more nearly perfect than are those of rock salt, it is natural to choose calcite for our basis of wave-length measurements. It is a fortunate, though largely fortuitous circumstance that the value which we obtain for the grating space of calcite at 18° is identical with that employed by Siegbahn, namely 3.02904 A. Thus as far as the grating space is concerned our results suggest no correction whatever to his values.

In order to get absolute wave-length measurements it is of course necessary to take into account the refraction of the x-rays in the diffracting crystal. As Ewald and others have shown, if the x-rays are of considerably higher frequency than the maximum critical frequency of the diffracting crystal, this correction can be made by merely altering slightly the grating space.[25] In this case[26]

$$\delta = ne^2\lambda^2/2\pi mc^2, \tag{4}$$

where n is the number of mobile electrons per unit volume of the crystal, e, m and c have their usual meaning, and λ is the wave-length of the incident rays. If the number of effective electrons per atom is equal to the atomic number, this becomes for calcite[27]

$$\delta = 3.67\lambda^2 \times 10^{-6}$$

if λ is expressed in angstroms. If this value is substituted in Eq. (2),

[22] M. Siegbahn, "Spektroskopie der Roentgenstrahlen," p. 20 (1924).

[23] W. P. Davey, General Electric Review, **27**, 744 (1924).

[24] Cf A. H. Compton, Phys. Rev. **11**, 431 (1918); M. de Broglie, "Les Rayons X" p. 34 (1922); and especially M. Siegbahn, "Spektroskopie der Roentgenstrahlen," p. 87 (1924).

[25] P. P. Ewald, Phys. Zeit. **21**, 617 (1920).

[26] A. H. Compton, Phil. Mag. **45**, 1123 (1923).

[27] A. H. Compton, l.c.[26] p. 1129.

noting that $\sin\theta = n\lambda/2D$ to a sufficient approximation, we obtain

$$n\lambda = 2D\sin\theta(1-0.0000147\ D^2/n^2). \qquad (5)$$

The true wave-length may then be calculated from Eq. (1) if, for the first order of reflection from calcite, we use an effective grating space of $3.0291\ (1-0.000135) = 3.0287$ A.

For rock salt the corresponding correction factor is $(1-0.000096)$. That is, to find the true wave-length we must use for the first order spectrum an effective grating space of 2.8144 A at 20°C.

As a typical case of the determination of absolute wave-length we may consider the $K\alpha_1$ line of molybdenum. Using 3.02904 A as the grating space of calcite at 18°, Siegbahn gives for this wave-length[28] 0.70759 A. Though our present work gives the same value for the true grating space, the correction due to refraction changes[29] the effective grating space for the first order spectrum to 3.02864, reducing the wave-length to 0.70749 A.

We accordingly recommend the following values as the most probable in light of this investigation:

$$D(CaCO_3) = (3.0291 \pm .0010) \times 10^{-8} \text{ cm at } 20^\circ \text{ C.}$$

$$D(NaCl) = (2.8147 \pm .0009) \times 10^{-8} \text{ cm at } 20^\circ \text{ C.}$$

Mo $K\alpha_1$ line, $\lambda = 0.70749 \pm .00023$ A.

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January 31, 1925

[28] M. Siegbahn, "Spektroskopie der Roentgenstrahlen," p. 102 (1924).

[29] Professor Siegbahn informs us that he has applied a correction of this character to some of his most recent wave-length determinations.

THE RELATIVE MOBILITY OF INITIAL POSITIVE IONS IN GAS MIXTURES AT LOW PRESSURES

By H. B. Wahlin

Abstract

The relative mobilities of the initial positive ions in gas mixtures at pressures of 30 to 60 mm have been determined for mixtures of C_2H_5Cl and H_2, N_2 and H_2, and N_2 and C_2H_5Cl, using the Franck-Rutherford alternating potential method and ions produced by α-rays of polonium. High frequency potential generated by a Hartley oscillator was used so as to insure that the age of the ions was only a fraction of a second. In each case two types of ions were detected, for which the ratio of the mobilities came out equal to the inverse ratio of the square root of the molecular weights. These ratios were found to be independent of the relative amounts of the gases present, although the absolute values of the mobilities changed. This would seem to indicate that the initial mobility at low pressures is determined chiefly by the mass of the ion rather than by its dimensions. The fact that aged ions have lower mobilities indicates that they are clusters.

Introduction

RECENT experiments on ionic conduction in gases have indicated that the ordinary gaseous ions are not simply charged molecules, but that they consist of charged molecules or atoms to which are attached neutral molecules, in this way forming a cluster.

Thus Erikson[1] and the writer[2] have demonstrated the existence in air of two types of ions having mobilities of 1.35 and 1.89 cm/sec/volt/cm. It was found furthermore that if the 1.89 ion was aged for a sufficiently long time it would pass over into the 1.35 type. It is impossible to say at present just how much time is necessary on the average for a transition of the one type of ion into the other. Erikson estimated that if the ions were aged for one-half a second, the transition would be complete. The formation of the cluster, therefore, does not take place immediately after the molecule is ionized, but apparently only after a number of impacts with the neutral molecules. Nolan[3] has been able to obtain not only the mobilities given above, but larger values as well.

In order to throw more light on the question of the nature of gaseous ions, investigators have measured the mobility of ions of different types in air and in other gases to determine if a distinction could be found

[1] H. A. Erikson, Phys. Rev. **20**, 117 (1922)
[2] H. B. Wahlin, Phys. Rev. **20**, 276 (1922)
[3] J. J. Nolan, Proc. Roy. Irish Acad. **36**, A 5, 74 (1923)

between the mobilities of these different ions in a given gas. Rutherford[4] and Franck[5] have measured the mobility of the recoil atoms of radioactive disintegration in an atmosphere of air, and have found no sensible difference between this mobility and the mobility of the normal air ion. More recently Erikson[6] has determined the mobility of the actinium B ion in air, and has found two values, 3.15 and 1.2 cm/sec/volt/cm. Wellisch,[7] using a modification of the Langevin method, attempted to distinguish between the mobilities of different types of ions in gaseous mixtures, but was unable to detect any difference. He also attempted to determine the mobility of the methyl iodide ion in hydrogen, and concluded that its mobility was the same as that of the hydrogen ion.

More recently Grindley and Tyndall,[8] using a modification of the air stream method have determined the mobility of the negative and positive ions of hydrogen, ammonia, carbon dioxide, ether and chloroform in air, and have found that the mobility of the ion is the same as the air ion in each case to well within one per cent. While some question might be raised in regard to the results on the negative ions, since at least in the case of hydrogen it is questionable if the negative ion exists, there seems to be no doubt that in the case of the positive one of each gas the mobility is the same as the normal air ion at atmospheric pressure. In all these experiments no attempt was made to distinguish between the initial and the final ion.

Erikson[9] has verified the conclusions of Grindley and Tyndall in the case of carbon dioxide, and has extended them in that he has shown that the mobility of the unaged ions of CO_2 in air is the same as the unaged air ions in air.

Since all these experiments were performed at atmospheric pressure, it seemed advisable to the writer to undertake a determination of the mobilities in gas mixtures at lower pressures to see if the conclusions to be drawn from the experiments cited above are valid for initial ions under these conditions.

Method and Apparatus

The method used was the Franck modification of the Rutherford alternating potential method, and has been described in detail in the

[4] Rutherford, Phil. Mag. **5**, 95 (1903)
[5] Franck, V. Deut. Phys. Ges. **5**, 397 (1909)
[6] H. A. Erikson, Phys. Rev. **23**, 778 (June 1924)
[7] E. M. Wellisch, Proc. Roy. Soc. **82**, 500 (1909)
[8] Grindley and Tyndall, Phil. Mag. **48**, 711 (Oct. 1924)
[9] H. A. Erikson, Phys. Rev. **24**, 502 (Nov. 1924)

paper referred to above.[2] The ions were generated by the α particles from polonium in an auxiliary chamber, and were driven by a field through a gauze. It was found necessary to investigate the unaged ions only so as not to complicate the curves by the presence of many types of ions. This field was of sufficient strength, therefore, so that the interval that elapsed between the formation of the ion and the time it reached the gauze was well below 1/100 sec. which is small compared with the estimated time of aging. Between the gauze and a collecting plate accurately parallel to the gauze and connected to an electrometer, an alternating potential was established. The alternating potential was furnished by a Hartley vacuum tube oscillator, and had a frequency which could be varied from 200 cycles/sec. to as high a value as was desired.

In order that the nature of the ions should not change after passing through the gauze, the frequency and consequently the alternating potential was kept as high as could be measured accurately so that the time the ions spent between the gauze and the collecting plate was short compared with the estimated aging time.

Curves were obtained for mixtures of ethyl chloride and nitrogen, ethyl chloride and hydrogen, and nitrogen and hydrogen. The nitrogen and hydrogen were freed from oxygen by passing them over hot copper, and dried by passing through calcium chloride and phosphorous pentoxide. The ethyl chloride was obtained from tubes such as are used in medicine, and was redistilled and dried with phosphorous pentoxide.

The procedure was the usual one of measuring the current to the electrometer for different values of the alternating potential, and from the data obtained plotting a curve of the current against voltage.

Obviously if one type of ion only is present, a smooth curve with a definite voltage intercept should be obtained. If more than one type, each with a different mobility, are present, the resulting curve should show definite breaks, the voltage corresponding to a break representing the potential at which one type of ion just succeeds in reaching the collecting plate. The mobility could then be computed from the breaks as well as from the intercept by the relation

$$u = \pi n d^2 / \sqrt{2} V \tag{1}$$

where n is the frequency, d is the distance between the gauze and the collecting plate, and V is the effective value of the alternating voltage.

Experimental Results

Figs. 1, 2, and 3 show samples of curves obtained in mixtures of ethyl chloride and nitrogen, ethyl chloride and hydrogen, and nitrogen and

hydrogen respectively at pressures ranging from 30 to 60 mm. Each of these curves shows a definite break which indicates the presence of one type of ion in addition to the one corresponding to the intercept. With only one gas in the ionization chamber, only one type of ion was in evidence. These breaks could be repeated at will, therefore they cannot be ascribed to irregularities in the electrometer readings. The ordinates of curve 1, Fig. 2, have been displaced upward. There are strong indications

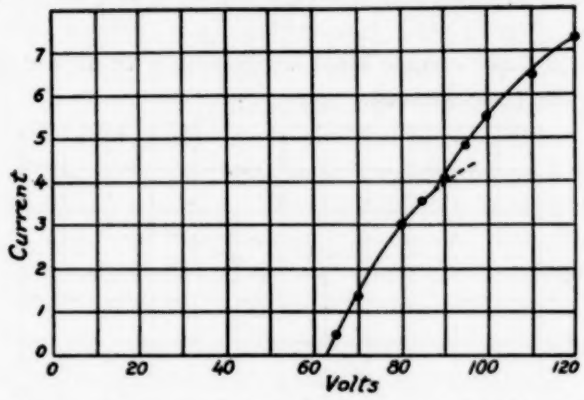

Fig. 1. Current voltage curve with mixture of ethyl chloride and nitrogen.

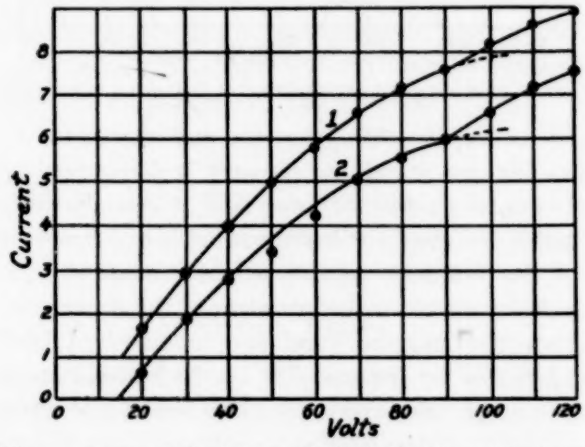

Fig. 2. Curves withmixtures of ethyl chloride and hydrogen.

of a break at about 57 volts on curve 2 of this figure, but as will be noted this is entirely absent in curve 1, nor did it appear in any other of the curves, and it was, therefore, ascribed to irregularities in the electrometer readings.

The ratio of the two mobilities from any curve is the same as the inverse ratio of the voltages, as is shown by Eq. (1). On the assumption that

the lower mobility corresponds to the heavier ion, the ratio of the mobility from the intercept to that from the break was found to be very nearly the same as the inverse ratio of the square roots of the molecular weights of the gases, as may be seen from the following table:

Gases	Ratio of mobilities	Ratio of square roots of molecular weights
H_2 and C_2H_5Cl	5.79	5.66
H_2 and N_2	3.75	3.74
N_2 and C_2H_5Cl	1.49	1.51

This ratio did not change measurably with a change in the relative amounts of the gases present.

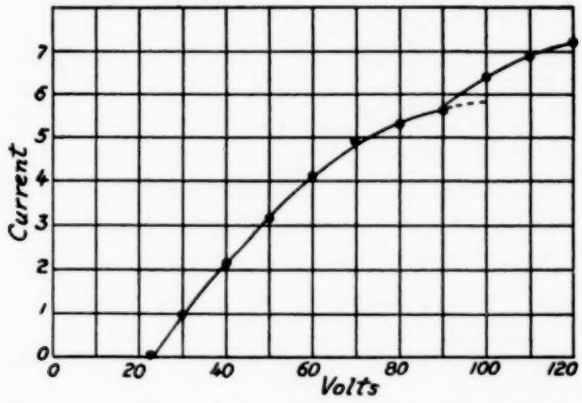

Fig. 3. Curve obtained with mixture of nitrogen and hydrogen.

The indications are, therefore, that the mobility of the *initial ion* in any gas or gas mixture at reduced pressure is determined primarily by the mass of the ion, and not by its dimensions. Certainly the fact that the ratio of the mobilities is approximately equal to the inverse ratio of the square root of the molecular weights would indicate this.

That the mobility should be independent of the dimensions of the ion has been suggested by Langevin,[10] and more recently by Loeb.[11] Langevin derived an expression for the mobility on the basis of an inverse fifth power law of force between the ion and molecule, and obtained

$$u = \frac{.505}{\sqrt{(K-1)\rho}} \sqrt{1 + \frac{m}{M}}$$

where K is the dielectric constant of the gas, ρ is its density, m is the mass of a molecule, and M is the mass of the ion. This equation, while it shows that the mobility is independent of the dimensions of the ion,

[10] P. Langevin, Ann. de Chem. et de Phys. **5**, 283 (1905)
[11] L. B. Loeb, Phil. Mag. p. 446, Sept. 1924.

fails to predict the observed ratio of the mobilities as given above. Langevin points out, however, that in the derivation of this equation he has assumed that the ion suffers loss of momentum only because of the attractive forces between it and the molecules and not because of actual impacts. If the attraction is of the nature of an inverse fifth power law, a transfer of energy as a result of impacts might readily play an important part. It is possible that an equation taking both these means of transfer into consideration would satisfy the experimental results more closely. However, a complete analysis would be difficult to obtain as it would probably have to take into account what might be termed a statistical clustering of the surrounding gas about the ion due to the polarization of the gas by the field of the ion. It would furthermore have to take into consideration any deviation from the inverse fifth power law of force as the distance between the ion and the molecule becomes small.

The results presented here are not in agreement with those obtained for aged ions by Wellisch and others. Since Erikson found the same mobility for the initial CO_2 ion in air as for the initial air ion in air, the peculiarities of the present results are possibly due to the decreased pressure and not to the fact that initial ions were used.

In a recent article[12] the writer has extended the results on the aging in air, and has shown that if the aging time is increased above that used in the earlier experiments of the writer, the mobility decreases below the 1.35 value. The values found may be represented with a considerable degree of accuracy by the equation

$$u_n = 1.89\sqrt{2/(2+n)} \qquad (2)$$

where n has the values 0, 1, 2, 3, 4, 6. If it is assumed in accordance with the results presented in this paper that the mobility varies inversely as the square root of the mass of the ion, we may write

$$u_n = u_0\sqrt{M_0/M_n}$$

where M is the mass of the ion. If it be assumed also that the initial ion (mobility 1.89 cm/sec/volt/cm) consists of 2 atoms, and if we let n be the number of atoms added to this initial ion in the aging process, the above equation reduces to the same form as Eq. (2) above. The values of the mobility observed would then correspond to ions consisting of 2, 3, 4, 5, 6 and 8 atoms.

UNIVERSITY OF WISCONSIN,
MADISON, WISCONSIN,
December 3, 1924

[12] H. B. Wahlin, Phil. Mag. (March 1925) p. 566.

THE ABSORPTION COEFFICIENT FOR SLOW ELECTRONS IN GASES

By Robert B. Brode

Abstract

Electrons from a heated filament were accelerated through a slit and deflected magnetically around a circular path into a Faraday cylinder connected to a galvanometer. From the plots of the logarithm of the ratio of the galvanometer current G to the total electron current M from the filament, as a function of the pressure, the absorption coefficients were determined for various accelerating voltages from 2 to 360. For a given voltage, the absorption coefficient was found to be independent of the current M and also of the pressure (at about 10^{-2} mm). The results of Mayer and Ramsauer were checked for *argon* and *helium*. In argon, the coefficient reaches a sharp maximum at about 12 volts, the value for 2 volts being only one-fifth of the maximum value. In helium there is a maximum at 4 volts. *Methane* gave a curve similar to these, with a maximum at about 7.5 volts, which is in agreement with the results of Akesson. The curves for *nitrogen* and *carbon monoxide* are nearly identical, both having a maximum at about 18 volts and a minimum at about 9 volts. The curve for *hydrogen* shows no maximum, the coefficient increasing steadily down to 2 volts.

THE absorption of electrons in gases is due to the formation of negative ions and to the reflection from molecules. The electron is considered as absorbed when it disappears from the original beam by a change of its direction of motion or by loss of energy. The dependence of this absorption on the velocity of the electrons was first investigated by Lenard.[1] With an apparatus similar to that used by Lenard, Niels Akesson[2] found that the absorption in methane was a maximum at 8 volts, and that the slower electrons were much less absorbed. He found no selective absorption in hydrogen. The other gases which he investigated, CO, CO_2, C_3H_6, N_2O, N_2, and O_2 all indicated two maxima in their absorption curves.

The absorption coefficient for slow electrons in gases has been measured by C. Ramsauer[3] and H. F. Mayer.[4] These observers found that the absorption coefficients for hydrogen, nitrogen, helium and neon remained nearly constant, usually decreasing a little as the velocity of the electrons was increased. For argon they found that the absorption coefficient had

[1] P. Lenard, Ann. der Phys. **12,** 714 (1903)
[2] Neils Akesson, Lund's Acta N. S., 2, **12,** No. 11 (1916).
[3] C. Ramsauer, Ann. der Phys. **64,** 513 (1921).
[4] H. F. Mayer, Ann. der Phys. **64,** 451 (1921).

a maximum value at 13 volts. As the voltage was decreased below 13 volts, the value of the absorption coefficient decreased steadily until at 0.7 volt, their lowest observation, it was 1/30th of its maximum value. With increasing voltage above 13 volts the absorption coefficient steadily decreased.

Minkowski and Spooner[5] predicted from an experiment on the effect of gas on the space charge about a hot filament, that krypton and xenon should show this same phenomenon. Subsequent observations by Ramsauer[6] verified their prediction. The maxima in these gases were even more pronounced than in argon. G. Hertz,[7] by a method similar to that used by Mayer, confirmed the variation of the absorption coefficient in argon with changes of the velocity of the electrons. Townsend and Bailey[8] obtained data from the diffusion of electrons through argon that indicated very small values of the absorption coefficient for slow speed electrons.

The method used by Ramsauer to obtain a beam of uniform velocity electrons was used in this investigation. A series of slits were arranged on a circle and some of the electron paths were bent into this circle by a magnetic field. The radius of the circle in which a uniformly moving electron moves due to a magnetic field is given by the equation, $H \cdot r = 3.3\sqrt{V}$, where H is the magnetic field strength in gauss, V the energy of the electron in equivalent volts and r the radius of the path in centimeters. By making the slits narrow in comparison with the radius of the circle a beam of electrons could be obtained with practically uniform velocity.

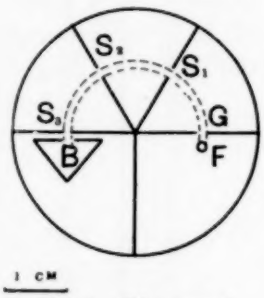

Fig. 1. Diagram of apparatus.

Apparatus

The apparatus used is shown in Fig. 1. It was made of copper parts silver-soldered together. The source of electrons was the filament F, a helix of tungsten wire usually operated at about 1.2 amp. The potential drop across the filament was then about 4 volts. The current for the filament was supplied by a storage battery maintained at a negative potential with respect to ground. The filament was placed 1 mm from the grid G which contained 10 holes 1 mm in diameter. The slits S_1, S_2

[5] Minkowski and Spooner, Zeits. f. Phys. **15**, 399 (1923)
[6] C. Ramsauer, Jahrb. Rad. u. Elek. **19**, 345 (1923)
[7] G. Hertz, Proc. Amsterdam Acad. **25**, 80 (1922)
[8] Townsend and Bailey, Phil. Mag. **44**, 1033 (1922).

and S_3 were rectangular, 1 mm wide and 1 cm high, and placed with their centers on a circle 1 cm in radius. The slits, grid and enclosing box were soldered together and connected to ground. A micro-ammeter measured the total emission of the filament and this reading, M, was taken as proportional to the electron stream that started around through the slits. The electrons that reached the box B went to ground through a galvanometer G, which measured the electron stream at the end of the path. The length of the path was 3.2 cm. The magnetic field that bent the electron stream into the circular path was produced by a solenoid 15 cm in diameter and 30 cm long, in which a current of 1 ampere produced a field of 19 gauss.

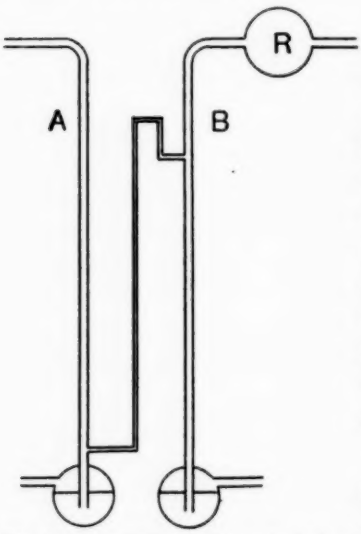

Fig. 2. Arrangement for admitting small quantities of gas.

Pyrex glass was used in the construction of the apparatus so that the copper parts could be baked out to 450°C. The vacuum was obtained by two mercury diffusion pumps in series, backed by an oil pump. To avoid gases from stop cock grease, mercury cut-offs were used in the high vacuum parts of the glass apparatus. These were separated from the part of the system containing the copper apparatus by a liquid air trap. A McLeod gauge, reading to 1×10^{-6} mm of Hg, was used to measure the pressure.

To admit small quantities of gas an apparatus shown in Fig. 2 was used. By adjusting the height of the mercury column A and lowering the column B, a known volume of 1 mm capillary tubing was filled with gas from the reservoir R. The pressure of the gas in R was usually about 1 or 2 cm of Hg. By raising the level of the mercury in B, this amount of gas could be forced into the space above A, which was connected to the high vacuum. In this way one could easily introduce just enough gas to make the pressure in the apparatus 1×10^{-3} mm of Hg, by changing the height of A and the pressure in R, the range of pressure produced by each operation could be varied indefinitely.

Method

If I_0 is the initial number of electrons in a beam sent through the gas and I the number still in the beam after it has passed through a distance x in the gas at a pressure p, then

$$I = I_0 e^{-\alpha x p}$$

where α is the absorption coefficient for the electrons at unit pressure of the gas. It is the total effective absorbing area in square centimeters of all the molecules in a cubic centimeter of gas at a pressure of 1 mm of Hg, when x is given in cm and p in mm of Hg. The effective absorbing area of a single molecule may be found by dividing α by 3.65×10^{15}, the number of molecules in a cubic centimeter of gas at a pressure of 1 mm of Hg.

By taking two sets of readings at different pressures two equations are obtained,

$$I_1=I_{01}e^{-\alpha x p_1} \quad \text{and} \quad I_2=I_{02}e^{-\alpha x p_1}$$

Solving these two equations for α gives,

$$\alpha=\frac{1}{x(p_1-p_2)}\log\left(\frac{I_1}{I_2}\cdot\frac{I_{02}}{I_{01}}\right).$$

In this equation only the ratio of the initial currents and of the final currents occur. The two readings of the micro-ammeter M, are proportional to the initial currents in the two cases and hence the ratio of the two readings may be used in place of the ratio I_{02}/I_{01}. The ratio of the two galvanometer readings is also equal to the ratio I_1/I_2.

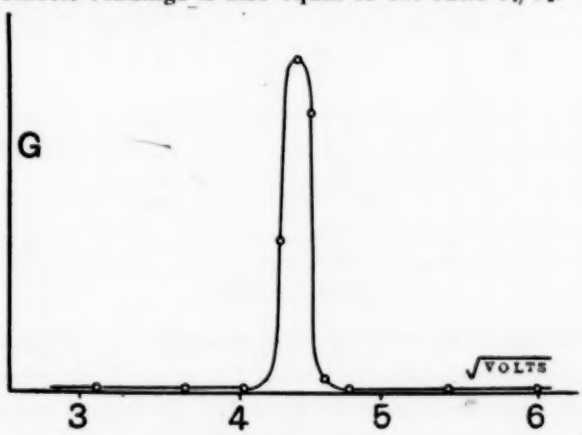

Fig. 3. Variation of the galvanometer deflection with square root of the accelerating potential, with constant magnetic field.

Because of the width of the slits, the voltage drop along the filament and the temperature distribution of velocities, galvanometer deflections were obtained for a range of values of the accelerating potential for a fixed value of the magnetic field as shown in Fig. 3. The reading M corresponding to the maximum deflection G of the galvanometer was recorded. A small quantity of gas was introduced, its pressure measured on the McLeod gauge and the corresponding readings of M and G recorded. If

the value of the log (M/G) is plotted against the product of the pressure and the distance, then α will be the slope of the line connecting any two observations taken at different pressures. Fig. 4 shows that α is practically independent of the pressure. The value of α was also found to be independent of the density of electrons in the beam. When M was increased from 1 to 5×10^{-4} amp., α remained constant.

Results

Argon, supposed to be 98 per cent pure, was taken from a bulb secured from the General Electric Co. The results of the measurements of α are shown in Fig. 5. The square root of the accelerating voltage is used as the abscissa because the velocity of an electron is proportional to the square

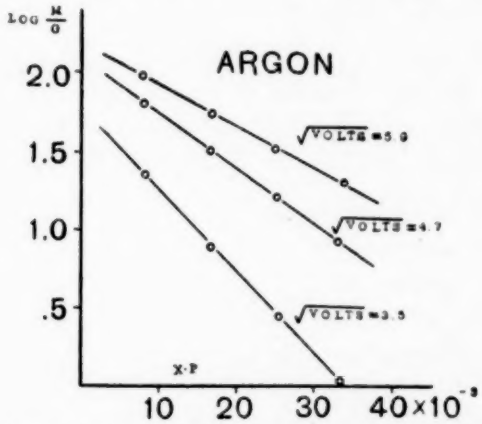

Fig. 4. Log of ratio of electron emission to maximum galvanometer deflection as a function of product of length of path and pressure, for three accelerating potentials in argon.

root of the voltage. The value of α was measured for velocities from 2 to 360 volts. The results obtained were found to check reasonably well with those obtained by Ramsauer, shown by the dotted curve.

Helium was obtained from the U. S. Government. It was further purified by passing it through a charcoal tube immersed in liquid air. The charcoal tube had previously been heated for several hours at 450°C. The results are shown in Fig. 5. Ramsauer's results are indicated by the dotted curve.

Methane, obtained from natural gas, was furnished by Dr. Glockler of the Gates Chemical Laboratory of this institute. It was further purified by liquifying with liquid air and then distilling. From Fig. 5 it can be seen that the curve is similar to that found for argon. The maximum absorption at 7.5 volts agrees very well with the value of 8 volts found

previously by Akesson. The pressure of the gas did not change when allowed to stand in the presence of the hot tungsten filament. If the gas were decomposed by the temperature of the filament an increase in the pressure should be observed.

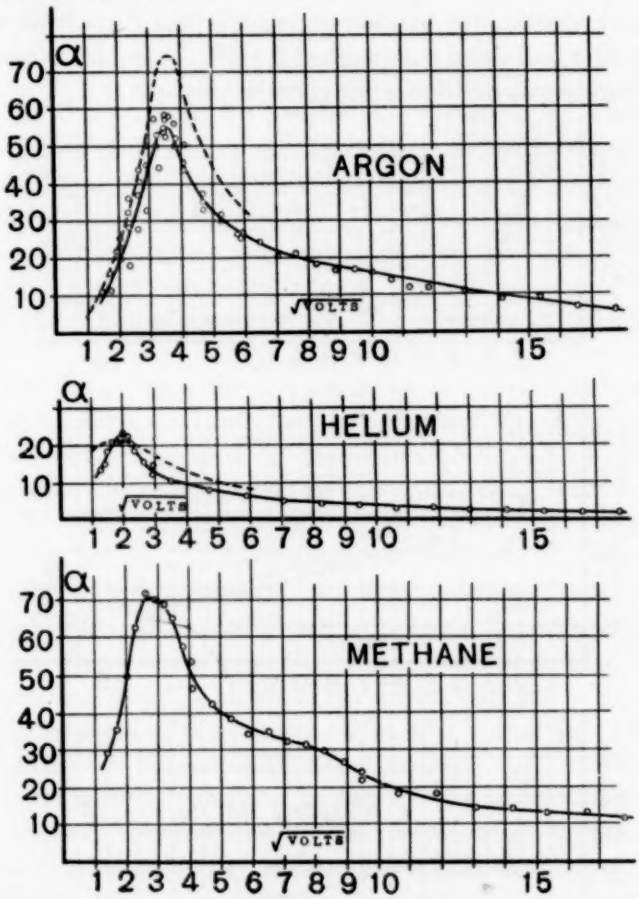

Fig. 5. Variation of absorption coefficient α in argon, helium and methane, with the velocity of electrons.

Hydrogen was dried and further purified by charcoal cooled with liquid air. Fig. 6 shows the values of α observed for hydrogen. The results are not in very good agreement with those of Ramsauer, shown by the dotted line. No maximum was observed in either case.

Nitrogen was prepared by the decomposition of ammonium nitrite. A water solution of this was heated and the resulting gas dried by passing it through a phosphorous pentoxide tube. The curve for nitrogen, Fig. 6, differs from any previous curve in that it has both a maximum and a mini-

mum. The minimum occurs at 9 volts which is near the resonance potential of the nitrogen atom, and the maximum at 18 volts which is near the ionization potential of the nitrogen atom. The determination of the maximum and minimum points was not sufficiently accurate to attach much significance to their occurrence near these critical points. Akesson's data indicate a maximum at 2 volts. A second maximum was also observed but its position is not given in his paper.

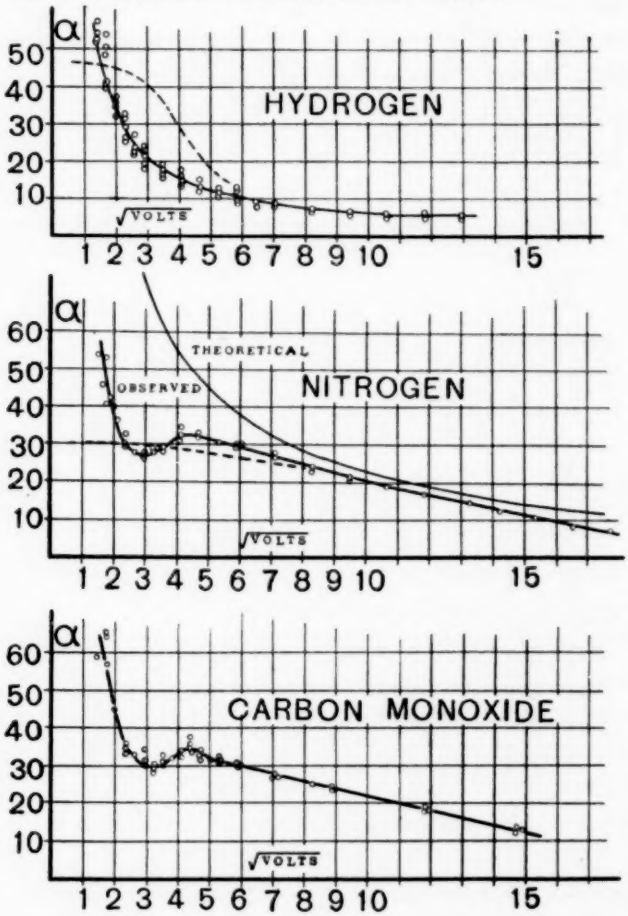

Fig. 6. Variation of α in hydrogen, nitrogen and carbon monoxide with velocity of electrons.

Carbon monoxide was prepared by the decomposition of formic acid on being dropped into hot sulphuric acid. The curve for carbon monoxide, Fig. 6, is seen to be almost identical with that obtained for nitrogen. The molecules of both gases consist of two atoms, each of which is supposed to have seven electrons. In the case of nitrogen the two positive

nuclei have each seven positive charges. In carbon monoxide one nucleus has six positive charges and the other eight. The similarity of the two curves indicates that the deflection of the slow speed electrons is determined chiefly by the field produced by the arrangement of the electrons in the molecule.

Theoretical Discussion

From the theory given by Zwicky[9] for the apparent absorption of electrons due to deflection in the field of a polarized molecule α should vary inversely as $\sqrt{V}$. Using the dielectric constant of nitrogen and the dimensions of the apparatus, $\alpha = 224/\sqrt{V}$. The relation between the computed and observed curves may be seen in Fig. 9. Using the dielectric constant of hydrogen and computing α, the above constant 224 is replaced by 150. This gives values of α that are about twice the observed values.

From this theory the value of α should never decrease with decreasing velocity of the electron. It can be shown that any attracting field that is independent of the orientation of the molecule will give a similar curve. For an inverse square attraction $\alpha = \text{const.}/V^2$; for an inverse cube law $\alpha = \text{const.}/V$; and for an inverse fifth power law $\alpha = \text{const.}/\sqrt{V}$.

Mayer[10] suggests as an explanation for the apparent maximum in nitrogen as observed by Akesson, that slow electrons in nitrogen have a selective reflection, i.e. do not attach so easily to the molecule to form a negative ion. But with the mean free path of the same order of magnitude as the total path length, one would not expect that half of the electrons would be reflected after two or more collisions into a collecting box whose opening subtended a small solid angle compared with the rest of the apparatus. A selective reflection for low velocity electrons requires that large numbers of negative ions should be formed at higher velocities. Because of their slower motion, the ions will remain in the beam for a comparatively long time and should have a large effect in increasing the effective absorption. Mayer found practically no change in α from 0.2 to 4 volts.

F. Hund[11] has proposed an explanation based on the quantum theory. He suggests that an electron whose kinetic energy is less than the amount of energy it would radiate if deflected, will not radiate but will continue undisturbed on its path. This explanation is suitable for the noble gases but will not explain the curves obtained for nitrogen and carbon monoxide.

[9] F. Zwicky, Phys. Zeit. **24**, 171 (1923).
[10] H. F. Mayer, Ann. der Phys. **64**, 474 (1921).
[11] F. Hund, Zeit. f. Phys. **13**, 241 (1923).

The number of ions formed, and consequently α, should increase as the density of electrons in the beam is increased. Measurements of α in nitrogen showed no such increase. The variation of α appears to be due to changes in the absorption coefficient and not to a selective reflection.

The author wishes to express his indebtedness to Dr. R. A. Millikan for suggesting this investigation and for his interest throughout the work.

NORMAN BRIDGE LABORATORY OF PHYSICS,
CALIFORNIA INSTITUTE OF TECHNOLOGY,
October 31, 1924

THE MOTION OF ELECTRONS BETWEEN COAXIAL CYLINDERS UNDER THE INFLUENCE OF CURRENT ALONG THE AXIS

By A. W. Hull

Abstract

Current from a large electrically heated filament to a coaxial cylindrical anode, limited by the circular magnetic field.—(1) *Motion of the electrons.* Richardson has shown that if the filament current is sufficiently large (or the plate voltage too small), its magnetic field should prevent electrons reaching the anode. The equation for the critical plate voltage is here derived in a simpler and more general form which holds for any degree of space charge. Electrons leaving the filament are deflected in the direction of the electron current in the wire and describe paths which are found, by approximate integration of the equations of motion, to be somewhat elongated cycloids. The dimensions of the paths are calculated for typical cases. No electrons reach the anode unless the plate voltage is above $V_c = 2(e/m)I^2[\log(R/r_0)]^2$ (neglecting small terms which involve the initial velocities). The *effect of space charge* is to elongate the cycloidal paths, but in practical cases the effect is small. The *effect of superposing an axial magnetic field H* is to add to V_c the critical potential $V_c' = \frac{1}{8}(e/m)H^2R^2$ due to the field H alone. This conclusion that the circular and axial magnetic fields act independently was fully verified experimentally. (2) *Plate current as a function of voltage.* Results for tubes with tungsten filaments 3/4 mm and 2.5 mm in diameter are given. The steep part of the curve points in each case to the theoretical critical voltage, but there is a foot extending to lower voltages, due to reflection and scattering of electrons. This foot is much less with a small anode (2.5 cm diam.) than with one four times the diameter. The *reflection effect* was directly proved with a special tube which enabled the current to various sections of the anode to be measured independently. If at a steep part of the curve an *alternating plate voltage is superposed*, the effective alternating current resistance is only about 35 ohms for a tube with 2.5 cm anode. (3) *Plate current as a function of filament current.* If the voltage is kept constant at a high enough value, and the filament current slowly increased, emission begins at a certain temperature and increases rapidly (temperature limited) and then decreases sharply to zero (magnetically limited). With a 2.5 mm filament in a 10 cm anode, for instance, for 800 volts potential the plate current is zero except for the range 130 to 200 amp., while for 1000 volts, it is zero except between 130 and 225 amp. *With an alternating filament current* the plate current is suppressed except during the part of each cycle when the instantaneous filament current is below the critical maximum. Thus the tube gives an intermittent unidirectional current of twice the frequency of the filament current. In a tube with filament 1 cm in diam. carrying 1600 amp. and anode 4.6 cm in diam. at 3100 volts, a plate current (space charge limited) of 45 amp. was completely controlled by the magnetic field of the filament current.

Experiments with Pring tube containing filament and metal disk.—The explanation offered by Langmuir in 1913 that the decrease of electron emission with improvement in vacuum observed by Pring and Parker was due to charge on the glass walls, is verified.

1. Introduction

THE magnetic field of heating current has frequently been mentioned as a factor which should be considered in electron tubes,[1] and the effect to be expected in cases where space charge is negligible has been calculated;[2] but no such effects have ever been observed, so far as I know.[3]

The effect is very small indeed with filaments of ordinary size (cf Tables I and II below), and is masked by the relatively enormous effect of the voltage gradient along the filament, due to the same current.

With very large filaments, on the other hand, the magnetic field of heating current may, as Richardson suggested, play an important role. The experiments here described show that in the case of symmetrical cylindrical electrodes and large heating currents the magnetic field is the most important factor, and effectively prevents electrons from reaching the anode, even with a very high anode potential. The value of heating current necessary to produce this effect is definite for each anode voltage, in agreement with theory.

2. Theory; Concentric Cylindrical Electrodes, Magnetic Field Due to Current Through Inner Cylinder

O. W. Richardson has calculated[1] the critical current necessary to prevent electrons from reaching the anode, for the case of infinitely long cylinders and negligible space-charge. In the analysis here given no restriction is placed upon space-charge or length. Symmetry is assumed, the electrodes being surfaces of revolution; and the leading-in wires to the inner cylinder are assumed straight and parallel to the axis for a sufficient length to insure uniformity of the magnetic field. The solution gives the same value of critical current as that found by Richardson, but in simpler form, and free from restrictions.

Using cylindrical coordinates r, θ, z, we shall let (see Fig. 1) X, 0, Z be the corresponding components of the electric field, and 0, $2I/r$, 0 be the components of the magnetic field.

[1] O. W. Richardson, Proc. Roy. Soc. A, **90**, 174 (1914); Richardson and Chaudhuri, Phil. Mag. **45**, 337 (1923); H. M. Freeman, Electric J. **19**, 501 (1922); W. H. Eccles, "Continuous Wave Wireless Telegraphy," Wireless Press Ltd., p. 297 (1921)

[2] O. W. Richardson, l.c.[1]

[3] The decrease of electron emission with gas pressure in Pring and Parker's experiments (Pring and Parker, Phil. Mag. **23**, 192, 1912; J. N. Pring, Proc. Roy. Soc. **89**, 344, 1914) was due to electrostatic effects, and not to the magnetic field of the heating current. These experiments are discussed in detail in section 15 below.

The equations of motion, for an electron starting from a point at distance r_0 from the axis, with initial velocity components u_0, v_0, w_0, are

$$\ddot{r}-r\dot{\theta}^2=X\frac{e}{m}+2I\frac{e}{m}\dot{z} \tag{1}$$

$$\frac{1}{r}\frac{d}{dt}(r^2\dot{\theta})=0 \tag{2}$$

$$\ddot{z}=Z\frac{e}{m}-\frac{2I}{r}\frac{e}{m}\dot{r} \tag{3}$$

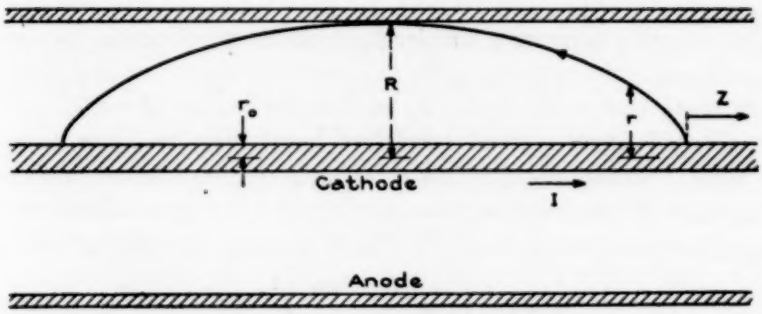

Fig. 1. Cross section sketch of cylindrical tube showing path of electron under the influence of electric field of anode and magnetic field of filament current.

Integration of Eqs. (2) and (3) with respect to time gives, respectively,

$$r^2\dot{\theta}=\text{const.}\ =r_0v_0$$

whence

$$\dot{\theta}=r_0v_0/r^2 \tag{4}$$

and

$$\dot{z}=w_0+\int_0^t Z\frac{e}{m}dt-2I\frac{e}{m}\log\frac{r}{r_0} \tag{5}$$

Substituting these values of $\dot{\theta}$ and $\dot{z}$ in Eq. (1), and integrating with respect to r, gives

$$\dot{r}^2=u_0^2+v_0^2\left(1-\frac{r^2}{r_0^2}\right)+2\frac{e}{m}\int_{r_0}^{r}Xdr+\left(2I\frac{e}{m}\right)^2\int_{r_0}^{r}\frac{1}{r}\int_0^t Zdtdr$$

$$-\left(2I\frac{e}{m}\log\frac{r}{r_0}\right)^2+4I\frac{e}{m}w_0\log\frac{r}{r_0}\cdot \tag{6}$$

The condition that an electron shall be turned back just before it reaches the anode is $\dot{r}=0$ when $r=R$, the radius of anode; also, by definition, $\int_{r_0}^{R} X dr = V$ (potential difference between cathode and anode) and[4]

$$\int_{r_0}^{r} \frac{1}{r} \int_{0}^{t} Z dt dr = \int_{0}^{t} \left(\int_{r_0}^{r} \frac{z}{r} dr \right) dt = 0.$$

Making these substitutions in Eq. (6) and solving for V, one obtains, as the condition that an electron shall just fail to reach the anode,

$$V_c = 2\frac{e}{m}\left(I \log \frac{R}{r_0} - \frac{m w_0}{2e} \right)^2 - \frac{m}{2e}\left(u_0^2 + w_0^2 + v_0^2 \left[1 - \frac{r_0^2}{R^2} \right] \right). \tag{7}$$

This equation assumes a simpler form under experimental conditions. The radius r_0 of the cathode, under practical test conditions, is of the order of one tenth that of the anode R, so that the bracket $[1-r_0^2/R^2]$ which multiplies v_0^2 (itself a small correction term) may be taken as unity. The term in initial velocities then becomes the total initial energy per unit charge of the electron, viz., $\frac{1}{2}(m/e)(u_0^2+v_0^2+w_0^2)$. Representing this by its equivalent potential V_0, Eq. (7) becomes, for all practical cases,

$$V_c = 2\frac{e}{m}\left(I \log \frac{R}{r_0} - \frac{m w_0}{2e} \right)^2 - V_0 \tag{8}$$

where V_c = critical potential difference in electromagnetic units.
V_0 = initial velocity of electrons in equivalent potential units.
I = current through filament in e.m.u.
w_0 = component of initial velocity parallel to axis in cm per sec.
R, r_0 = radii of anode and cathode, respectively.

3. Approximation in Case of Large Filaments

For large values of $[I \log(R/r)]$, with correspondingly large values of V, the terms containing the initial velocities w_0 and V_0 are negligible, and Eq. (8) becomes

$$V_c = 2\frac{e}{m} I^2 \left(\log \frac{R}{r_0} \right)^2. \tag{9}$$

Changing to practical units of volts, amperes and the base of logarithms to 10, and inserting $e/m = 1.769 \times 10^7$, this becomes

$$V_c = .01876\, I^2 [\log_{10}(R/r_0)]^2. \tag{10}$$

Since the range of operating temperature for any given type of cathode is very narrow, the normal direct current I necessary to maintain this

[4] $Zdr = 0$ since dr is at right angles to Z. Likewise, since r is always finite, $(Z/r)dr = 0$

temperature can be expressed in terms of the diameter of the filament. Thus for tungsten filaments[5] at 2500°K, $I_{amp} = 1530\, d_{cm}^{3/2}$. Eq. (10) can therefore be written

$$V_e \text{ (volts)} = 352{,}000\, [\log_{10}(R/r_0)]^2\, r_0^3 \text{ (cm)}. \qquad (11)$$

4. Examples

Eq. (11) shows that the critical voltage increases as the cube of the cathode diameter, if the ratio of anode to cathode diameter is kept the same. For example, if the anode diameter is 10 times that of the cathode, a tube with a 1 cm diam. cathode will pass no current at voltages below 44,000 volts; a tube with a 1 mm cathode will begin to pass current at 44 volts; and a tube with 1/10 mm (4 mils) diameter cathode will have a critical potential of only .044 volts (approximate, since initial velocities are important in this case). These values are collected in Table I.

Table I

Critical voltages for tungsten filaments at 2500°K with direct current heating. Ratio of anode to cathode diameter = 10.

Diameter of anode	Diameter of cathode	Critical voltage
0.1 cm	.01 cm	.044 (approx.)
1.0	0.1	44.
10.0	1.0	44000

The critical voltage increases less rapidly than the cube of the cathode diameter when, as is more nearly practical, the anode diameter is kept constant, instead of the ratio of anode to cathode diameter. A few examples, shown in Table II, will give an idea of the critical voltages for different sizes of filament under these conditions. The values of critical voltage are calculated from Eq. (11), and refer to electrons starting from the cathode with zero initial velocity. The correction to be applied for initial velocities of 1 volt ($u_0 = v_0 = w_0 = \pm 6 \times 10^7$ cm/sec.) is given after each value of critical voltage. These corrections are calculated from Eq. (8), which, in practical units, takes the form

$$V(\text{volts}) = .01876[I(\text{amp.})\log_{10}(R/r_0) - 1.23 \times 10^{-7} w_0]^2 - V_0(\text{volts}) \qquad (8)$$

Table II

Critical voltages for tungsten filaments at 2500°K with direct current heating. Anode diameter = 5 cm

Diam. of filament	Critical voltage
0.0025 cm	0.0075 – 1.4
0.025	3.6 ± 4.
0.100	127. ± 23.
0.250	1140. ± 70
1.00	21600. ±300.
2.50	62300. ±500.

[5] Langmuir, Phys. Rev. 7, 302-30 (1916)

It will be noted that initial velocities of 1 volt affect the critical potential by 1 per cent even at 20,000 volts. This effect is due to the component of initial velocity parallel to the axis of the tube. Eq. (8) shows that the proportional effect of the w_0 term upon the critical potential is (approx.) $2\sqrt{mw_0^2/2e}/\sqrt{V}=2\sqrt{W_0/V}$, where W_0 is the component of initial velocity parallel to the axis in equivalent volts, while the proportional effect of the term representing the total velocity V_0 (in equivalent volts) is V_0/V. Thus when the total initial energy (in volts) is 1 per cent of the critical potential, the effect of the component parallel to the axis will be 20 per cent. This offers a possible method for further study of the tangential components of emission velocities, provided ambiguities due to reflection of electrons from anode and cathode can be avoided.

5. External Cathode

Eq. (7) applies also equally well to electrons traveling inwards from an external cathode to an internal anode, or to ions formed at a distance r_0 from the axis of the tube and traveling either inwards or outwards. When the electrons or ions travel inwards, r_0 in the above equations is to be taken as radius of the outer cylinder from which the electrons start, and R that of the inner cylinder. The numerical value of the ratio R/r_0 is, in this case, the inverse of what it would be if the electrons or ions started from the inner cylinder. The effect of this inversion on Eq. (7) is to change the sign of $\log (R/r_0)$ and to increase the multiplier of v_0^2. Neither of these changes affects appreciably the value of the critical potential; the change in sign of $\log (R/r_0)$ not at all, since negative values of w_0 occur as frequently as positive, and the increased value of the term in v_0^2 only slightly, since it still remains a small correction term. Hence the critical voltage will be the same for internal and external anode, except for the slightly larger correction (still small) for tangential initial velocities noted above.

It is also evident from Eq. (8) and the examples already given, that even the lightest ions will be entirely unaffected by the magnetic field of any attainable filament currents.

6. Combined Circular and Axial Magnetic Fields

It is easy to calculate the effect of an externally impressed uniform magnetic field H, parallel to the filament, superimposed upon the internally impressed field $2I/r$ due to the heating current. The electrodes are assumed as before to be concentric cylinders of revolution. Using cylindrical coordinates as before, the equations of motion are

$$\ddot{r}-r\dot{\theta}^2=X\frac{e}{m}-H\frac{e}{m}r\dot{\theta}+2I\frac{e}{m}\frac{\dot{z}}{r} \tag{12}$$

$$\frac{1}{r}\frac{d}{dt}(r^2\dot{\theta})=H\frac{e}{m}\dot{r} \tag{13}$$

$$\ddot{z}=Z\frac{e}{m}-2I\frac{e}{m}\frac{\dot{r}}{r} \tag{14}$$

where X, Z, are the components of electric field in the r and z directions respectively.

Integrating Eqs. (13) and (14) with respect to time, substituting the resulting values of the $\dot{z}$ in Eq. (12), and integrating this with respect to r, gives

$$\dot{r}^2=2\frac{e}{m}V-\left(r_0w_0-r_0^2\frac{He}{2m}\right)^2\left(\frac{1}{r^2}-\frac{1}{r_0^2}\right)-\left(\frac{He}{2m}\right)^2(r^2-r_0^2)$$
$$-\left(2I\frac{e}{m}\log\frac{r}{r_0}\right)^2+4I\frac{e}{m}\log\frac{r}{r_0}w_0+u_0^2. \tag{15}$$

Placing, as before, $\dot{r}=0$ when $r=R$ (radius of anode), as the condition that electrons shall just be able to reach the anode, and collecting terms, the critical voltage V_c is found to be

$$V_c=H^2\frac{e}{8m}R^2\left(1-\frac{r_0^2}{R^2}\right)+H\frac{r_0w_0}{2}\left(1-\frac{r_0^2}{R^2}\right)+2\frac{e}{m}\left(I\log\frac{R}{r_0}-\frac{mw_0}{2e}\right)^2$$
$$-\frac{m}{2e}\left(u_0^2+w_0^2+v_0^2\left[1-\frac{r_0^2}{R^2}\right]\right). \tag{16}$$

If V_c is of the order of 20,000 volts, all the terms containing initial velocities are negligible,[6] and Eq. (16) reduces to the very simple form

$$V_c=\frac{e}{m}\left[\frac{H^2R^2}{8}+2I^2\left(\log\frac{R}{r_0}\right)^2\right]. \tag{17}$$

Changing to practical units of volts, amperes, and inserting $e/m=1.77\times10^7$,

$$V_c=.0221H^2R^2+.0188I^2[\log_{10}(R/r_0)]^2. \tag{18}$$

V_c is the critical voltage, i.e. the voltage that is just sufficient to drag electrons from the cathode of radius r_0 to the anode of radius R, in the presence of the magnetic field due to I amperes flowing through the cathode combined with H gauss impressed parallel to the cathode.

It is to be noted that this critical voltage for the combined action of the two magnetic fields is the sum of the critical voltages of the respective

[6] See examples above and Phys. Rev. **18**, 34 (1921)

fields when they act separately [cf Eq. (10) above and Eq. (8), Phys. Rev. **18**, 34 (1921)].

7. Paths of the Electrons When Space Charge is Negligible

The differential equation of the path may be obtained at once from Eqs. (5) and (6) above. Neglecting initial velocities, and considering the central portion of the tube, where $Z=0$, these equations give

$$\dot{z}^2=[2I(e/m)\log(r/r_0)]^2$$

and

$$\dot{r}^2=2(e/m)V_r-[2I(e/m)\log(r/r_0)]^2$$

whence

$$\frac{dr}{dz}=\sqrt{\frac{V_r}{2I^2(e/m)\ [\log(r/r_0)]^2}-1}. \tag{19}$$

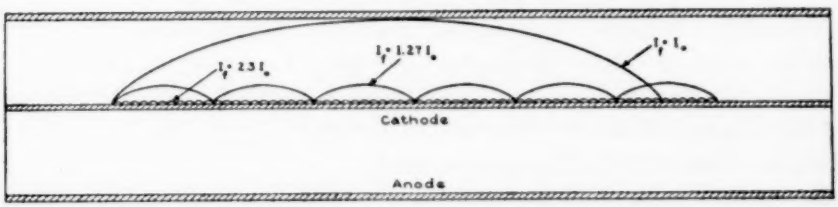

Fig. 2. Cross section of tube with 40 to 1 ratio of anode to cathode diameter, showing paths of electrons for three different values of current through the cathode, viz., critical current I_0, just sufficient to prevent electrons reaching anode; 1.27 I_0; and 2.3 I_0. In the last case the maximum radial excursion of the electrons is only 1/40 the distance from cathode to anode.

The path will therefore depend upon the degree of space-charge, which determines the potential distribution V_r.

8. *If space-charge is negligible*, the potential V_r is given by the electrostatic equation for concentric cylinders

$$V_r=[V_R/\log(R/r)]\log(r/r_0).$$

Combining this with Eq. (9) gives

$$V_r=2I^2(e/m)\log(R/r_0)\log(r/r_0). \tag{20}$$

In this R and V_R represent the radius and potential of the imaginary cylindrical surface at which the electron turns back. It may be any point between cathode and anode, depending upon the value of I.

Substituting V_r from (20) in Eq. (19) one obtains the very simple equation for the path of an electron, of zero initial velocity, moving in charge-free space between concentric cylinders of radii r_0 and R

$$dz=dr\sqrt{\log(r/r_0)/\log(R/r_0)}. \tag{21}$$

Eq. (21) is not directly integrable, but approximate solutions are easily obtained for given values of (R/r_0). Figs. 2 and 3 show typical paths, corresponding to $R/r_0=2$, 10, and 40; and Table III gives the distance traveled along the axis per jump, for a series of values of (R/r_0).[7]

TABLE III

Calculated distances along axis traveled by electrons, before returning to cathode, assuming negligible space-charge.

r_0 = radius of cathode; R = radius of imaginary cylinder to which path is tangent; z_0, z_1 = successive values of z (measured along axis) at which electron returns to cathode.

Ratio of radii R/r_0	Distance traveled along cathode. z_1-z_0	$\frac{z_1-z_0}{R-r_0}$
1.01	$.0314\times r_0$	3.14
1.1	.322	3.22
1.2	.657	3.29
1.3	1.005	3.34
1.4	1.360	3.40
1.5	1.720	3.44
2.0	3.716	3.72
3.0	8.154	4.08
5.0	18.16	4.54
10.0	46.60	5.11
20.0	112.4	5.92
40.0	251.2	6.42

It will be noted from Figs. 2 and 3 that the paths are of the general form of cycloids. For small ratios of (R/r_0) they are exactly cycloidal, as may easily be verified by replacing the logarithms in Eq. (21) by the first terms in their series expansions. This condition is very nearly satisfied for the smallest paths shown in Fig. 2. For larger values of R/r_0 the distance

[7] These values were obtained as follows.

For ratios of R/r_0 less than 1.5, Eq. (21) was put in the form

$$dz = Re^x(x-a)dx/\sqrt{ax-x^2};$$

where $x=\log(r/R)$; $a=\log(r_0/R)$.

Series expansion of e^x and term by term integration gave

$$z = Ra\sin^{-1}(1-2x/a)\left\{1-\tfrac{1}{2}(1-a)-(3a/8)\,(1-\tfrac{1}{2}a)-(5a^2/16)(\tfrac{1}{2}-\tfrac{1}{6}a)+\ .\ .\ \right\}$$
$$+R\sqrt{ax-x^2}\left\{(1-a)+(1-\tfrac{1}{2}a)\,(\tfrac{1}{2}x+3a/4)+(\tfrac{1}{2}-\tfrac{1}{6}a)\,(\tfrac{1}{3}x^2+5ax/12+5a^2/8)+\right\}$$

This gives results accurate to .1 per cent for $R/r_0 \leq 1.5$.

For ratios of R/r_0 greater than 1.5, the integration was performed in two stages. The first part of the path, for $r_0<r<.9R$, was obtained from step by step integration of Eq. (21), using Simpson's rule. The remainder of the path cannot be obtained in this way, since the function becomes infinite at $r=R$. It was obtained from the approximate equation

$$z=2R\sqrt{a}\left\{x-\tfrac{1}{5}x^2(1+1/2a)+\tfrac{1}{3}x^3(\tfrac{1}{2}+1/2a-1/8a^2)-\tfrac{1}{7}x^7(\tfrac{1}{6}+1/4a-1/8a^2+1/16a^3)+..\right\}$$

This equation is the integral of the series expansion of Eq. (21), which takes the form $dz=-2Re^{-x^2}\sqrt{a-x^2}$, upon substitution of $\log(R/r)=x^2$; $\log(R/r_0)=a$. It gives accurate results for $.7R<r<R$, for all values of R/r_0 greater than 1.5.

between intercepts becomes progressively greater than that of the cycloid, being approximately twice as great at $R/r_0=40$. (cf Table III and Fig. 2).

The most noteworthy feature in Fig. 2 is the rapid shrinking of the path with increase in heating current above the critical value. An increase in heating current of 27 percent above the critical value decreases the maximum excursion to 1/4, and for a heating current only slightly more than double the critical value the excursion is only 1/40 of the critical excursion. The shrinking is even greater when space charge is present, the maximum radial excursions corresponding to $I/I_0=1.27$ and 2.3 respectively being approximately 1/14 and 1/60 of the distance from cathode to anode (see next section).

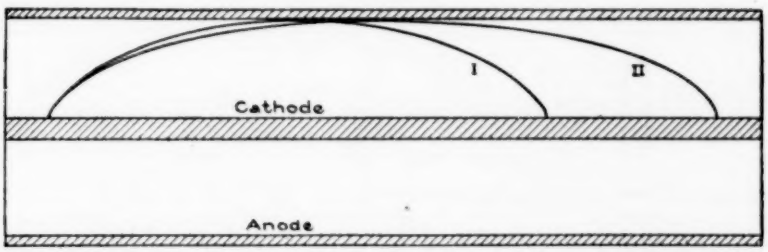

Fig. 3. Cross section of tube with 10 to 1 ratio of anode to cathode diameter, showing path of electron when just prevented from reaching anode by magnetic field of heating current. Curve I represents the path when space-charge is negligible (small emission from cathode), curve II when maximum space charge is present. The actual path will always be intermediate between these two, generally near curve I.

9. Paths of Electrons When Space-Charge is Present

The effect of the space charge is to weaken the electric field near the cathode, and hence to lengthen the path in the Z direction (parallel to axis). With maximum space-charge the field at the cathode is zero, and the path has its longest possible value. This condition seldom exists, however, since in all practical cases the degree of space-charge is far below the maximum that the space can hold under cut-off conditions, with full line voltage between cathode and anode. An exact solution of the path under maximum space-charge is therefore of little interest. An approximate solution, which is easily obtained, will serve satisfactorily as an upper limit to the length of path. The actual path will in most cases be nearer to the lower limit, which is the zero space charge case already discussed.

The approximate solution assumes the space-charge distribution given by Langmuir's equation[8] (for zero magnetic field)

[8] Langmuir, Phys. Rev. **2**, 450 (1913)

$$i=\frac{2\sqrt{2}}{9}\sqrt{\frac{e}{m}}\frac{V^{3/2}}{\beta^2 r}.$$

This distribution differs but slightly from the actual maximum space-charge in the magnetic field. To the same degree of approximation the factor β^2 may be taken as unity. This gives for the potential at any point r

$$V_r=V_R(r/R)^{2/3}. \tag{22}$$

Substituting this value of V_r in Eq. (19) one obtains, for the path of an electron of zero initial velocity moving between concentric cylinders of radii r_0 and R in the presence of maximum space-charge

$$dz=\frac{\log(r/r_0)dr}{\sqrt{(r/R)^{2/3}[\log(R/r_0)]^2-[\log(r/r_0)]^2}}. \tag{23}$$

This equation may be integrated in the same manner as Eq. (21), viz., step by step integration from $r=r_0$ to $r=0.9R$, and series expansion with direct integration from $.9R$ to R.[9] Fig. 3 shows the path calculated in this way, for a ratio R/r_0 of anode to cathode diameter equal to 10. It is almost identical in shape with the path for zero space charge, except that it is stretched 30 per cent in the z (axial) direction.

The actual path in all cases will lie between these two limiting paths, given by curves I and II in Fig. 3. Under practical conditions, the actual space charge will be only a small fraction, of the order of 1 per cent, of the maximum, so that the path will in most cases be very close to that represented by curve I.

The small relative space-charge is due to the combination of high voltage and small electrode spacing, requiring very large currents for full space-charge, and to the fact that most of the turned-back electrons are lost. The electrons hop up the filament, from negation to positive end, in the same direction as the conduction electrons in the filament. Hence upon their return to the filament they strike it with a velocity corresponding to the voltage-drop in the section of filament jumped, generally a considerable fraction of a volt, and most of them enter. This is in contrast to the action in the case of a magnetic field parallel to the filament, where the returning electrons strike the filament with only

[9] In order to obtain a rapidly convergent series the independent variable is changed to $x=\log(R/r)$. Eq. (23) then becomes $dz=-R(a-x)e^{-x}dx/\sqrt{a^2e^{-2x/3}-(a-x)^2}$, where $a=\log(R/r_0)$. Expansion of the right hand side of this equation in powers of x and integration gives

$$z=\frac{R}{c}\left\{2ax^{1/2}-(2/3)x^{3/2}(1+a-ka/2)+(2/5)x^{5/2}[1+a/2-k/2(1+a)+3k^2a/8]+\cdots\right\}$$

where $c=\sqrt{2a-(2/3)a^2}$; $k=1-(2/9)a^2(1-2x/9)/(2a-2/3a^2)$. This equation may be used from $r=R$ down to $r=.7R$

their emission velocities, or miss it entirely if it is small, so that full space charge eventually builds up even when the emission is quite small.

The degree of true reflection (without appreciable loss of energy) may be tested by its effect on the sharpness of cut-off. The electrons which just miss the anode will travel a considerable fraction of the length of the tube before returning to the cathode (cf Fig. 3). If then they are reflected without loss of energy they will emerge with initial energies of the order of magnitude of the whole potential drop in the cathode. Initial velocities of this order will have an enormous effect on the cut-off voltage (cf Eq. (8) and examples in Table II). The existence of such an effect was tested by the use of an equipotential cathode, which consisted of a nickel cylinder 1 cm in diameter, coated on the outside with barium oxide, with an insulated molybdenum core through which the heating current could be passed. The anode was a water-cooled copper tube of 1 inch inside diameter. No difference in volt-ampere characteristic could be detected when the potential drop in the cathode was changed from zero to that of the molybdenum core, indicating that reflection was not an important factor in this tube. The difference between anode and cathode diameter was so small in this tube that the paths were short and the voltage drop in the filament per path was only of the order of the Maxwell initial velocities. A more sensitive test with a larger diameter tube, divided into sections, is described below, and gives definite evidence of reflection.

Experimental Tests

10. *Tests with small filaments.* Filaments less than 20 mils ($\frac{1}{2}$ mm) diameter showed no measurable effect of magnetic field. The small effect that undoubtedly was present (cf Tables I and II) was obscured by the much greater effect of the voltage gradient due to the same current and inseparable from the magnetic field. With a 30 mil ($\frac{3}{4}$ mm) diameter filament and a large anode (10 cm diam.), the magnetic effect is well marked. Fig. 4 shows volt-ampere characteristics of such a tube, for two different values of filament current. Both characteristics differ from the theoretical space-charge characteristic shown in curve I, by an amount much greater than the voltage drop in the filament (13 and 21 volts respectively). The theoretical voltage at which measurable current should begin to flow to the anode, with 36 amperes filament current, as given by Eq. (8) with Maxwell's distribution of initial velocities, is shown at E_0. This agrees with the experimental value as closely as is to be expected, in view of the filament drop of 21 volts and a small "tail," always observed, due to electrons deflected by collision with gas molecules. The

lack of steepness of the curve above this voltage is due mainly to the shortness of the tube (see tests in section 11).

Fig. 5 shows a similar characteristic with a larger filament of 100 mils (2.5 mm) diam. in the same anode (10 cm diam. by 30 cm long). The characteristic for "zero heating current" was taken with the filament switch open, hence no magnetic field. With slight initial overheating of the filament there was ample time to read plate-current before the fila-

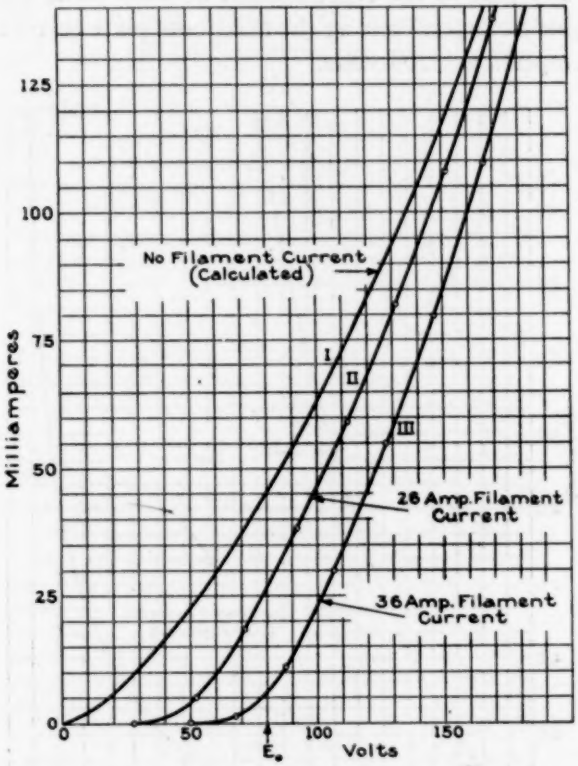

Fig. 4. Volt ampere characteristic of tube containing a 30 mil (.75 mm) filament in the axis of an anode 10 cm in diameter and 30 cm long. The calculated critical voltage for curve III is shown at E_0.

ment cooled down to normal temperature. This is the ordinary 3/2 power space-charge characteristic. The theoretical critical voltage, taking into account Maxwell initial velocities, is shown at E_0.

The effect of magnetic field is more striking when the filament current is varied, keeping anode voltage constant. Fig. 6 shows such a characteristic, and Fig. 7 a series of characteristics for different anode voltages, taken with the same tube as Fig. 5. As the filament temperature is slowly

raised, no emission occurs until the heating current reaches 130 amp. This is due to temperature limitation. From this point on the emisson rises rapidly according to Richardson's equation, entirely unaffected by magnetic field, to a definite maximum, e.g. 2 amp. at 1600 volts. With further increase of heating current the emission falls sharply and rapidly to zero. In this falling region the emission is controlled entirely by magnetic field, and is independent of temperature. Space-charge has no effect upon any part of the characteristic at 1600 volts, but becomes a factor at higher voltages, limiting the maximum plate current to approximately 10 amperes at 2200 volts.

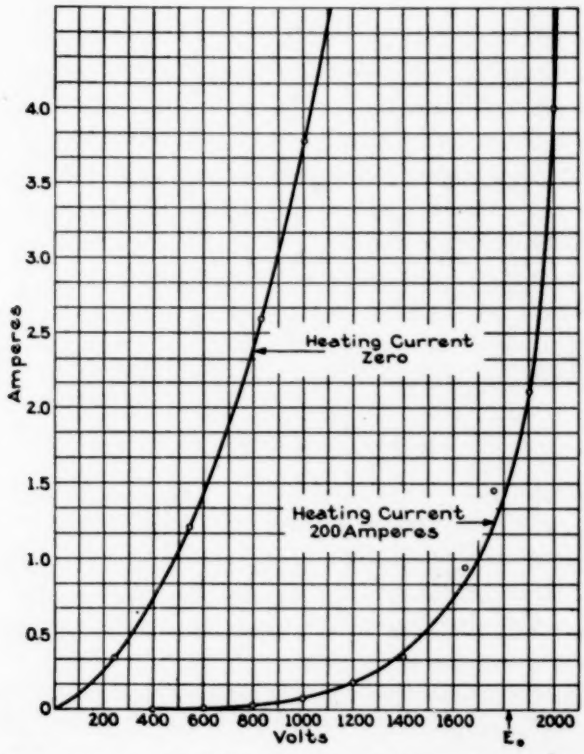

Fig. 5. Volt ampere characteristic of tube containing a 2.5 mm filament in axis of 10 cm diameter cylindrical anode. The calculated critical voltage for 200 amp. heating current is shown at E_0.

There is thus a definite range of filament current, narrower the lower the voltage, in which the tube will pass electron current. Below 700 volts no emission can be obtained at any steady filament current.

If the filament current is varied rapidly, as with alternating current, so that the filament remains at constant high temperature, the emission

is governed either by the instantaneous value of the heating current, or by space charge, according to which gives the lower value of emission. Fig. 8 shows a series of oscillograms taken in this way, with the same tube as Fig. 5, 6, and 7. The anode voltage was maintained constant. The lower curve B in each film is filament current, the middle curve A emission current from filament to anode. It will be noted that the emission is zero whenever the instantaneous value of filament current is above a critical value. Full space-charge current flows during that part of each cycle in which the heating current is below the critical value, and no current during the part when the field is above the critical value.

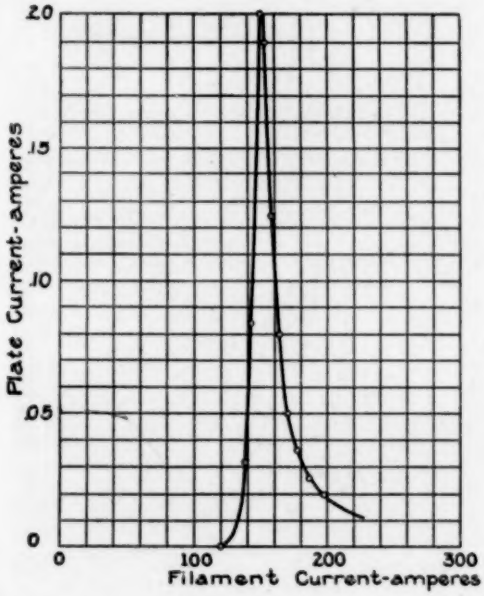

Fig. 6. Variation of plate current with filament current in a tube with 2.5 mm filament and 10 cm diameter anode at 800 volts.

The middle film was taken with a constant potential of 250 volts on the anode. During the greater part of each cycle the filament current is above the critical value for 250 volts, and the plate current is zero, as it should be. When the filament current falls to the value 73 amperes, plate current begins and increases rapidly to the maximum value allowed by space-charge. As soon as the filament current again reaches the same value of 73 amperes in the opposite direction, the plate current begins to fall, and drops rapidly to zero. The plate current is thus interrupted twice each cycle, since both directions of filament current are alike in their magnetostrictive effect.

The second (lower) film was taken with 505 volts on the plate. The space current is larger and flows for a longer part of each cycle, beginning and ending when the filament current reaches the value 101 amperes. The critical value given by Eq. (2) is 102 amperes. The filament current in this test (184 r.m.s. amperes) was larger than that used for the first film, and the lower curve shows distortion due to saturation in the filament transformer.

For the upper film a plate voltage of 1050 was used, and a larger filament current (201 amperes). The filament current curve shows bad saturation distortion, so that the distance from the point where it crosses

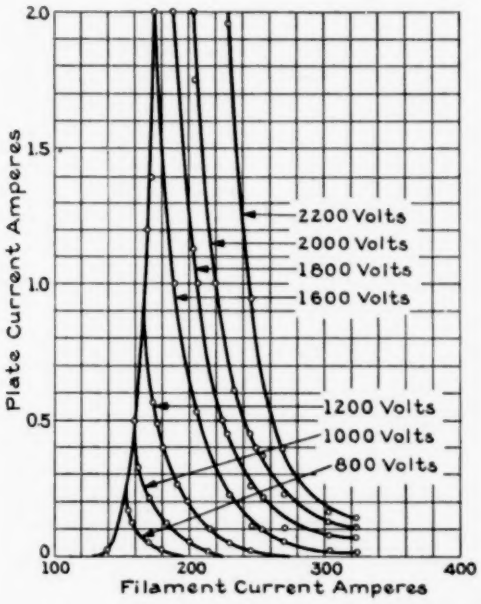

Fig. 7. Plate current-filament current characteristics of tube with 2.5 mm cathode and 10 cm diameter anode, at different (constant) anode potentials.

the axis to the point where it reaches its critical value is very different above and below the axis. In spite of this, the plate current begins and ends accurately at the critical filament current of 157 amperes, which agrees fairly well with the theoretical value of 149 amperes.

11. *Reflection of electrons at the cathode.* The "transition" current in Fig. 5, that is, the current at voltages below E_0, is larger than can be accounted for by gas collisions or lack of symmetry. It was suspected that this current was due to electrons reflected at the filament, which in this case, on account of the large tube diameter and consequent long paths (cf Fig. 2, which is drawn to scale for this tube) might have initial

velocities of the order of 10 volts. This hypothesis was tested by the following experiment. A tube was constructed with a 5 cm diameter anode divided into 3 sections, viz., a central section 15 cm, and two end sections each 5 cm long (Fig. 9). The cathode was a 100 mil (2.5 mm) tungsten wire, the same as in the previous test. All three anodes were

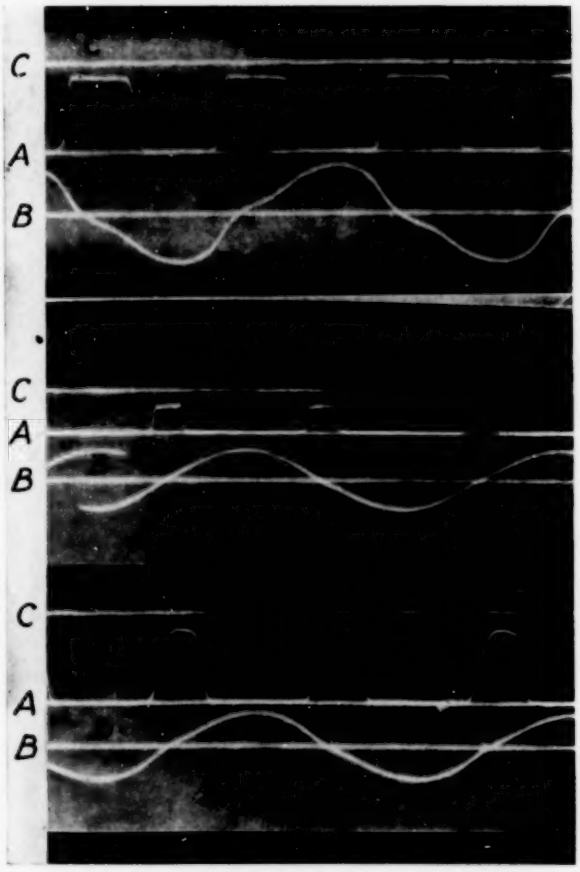

Fig. 8. Three oscillograms showing control of plate current by filament current, at constant plate voltage, in a tube with 2.5 mm filament and 10 cm diameter anode. In each film the lower curve B is filament current, and the middle curve A plate current. The upper curve (single line) is a calibration for the plate current curve.

maintained at the same voltage, and the current to each measured. Fig. 10 shows these currents as a function of voltage. Curves I, II, and III refer to the currents to sections 1, 2, 3, Fig. 9. It is seen that the current to section 1 (curve I) begins at approximately the correct voltage, but rises very slowly due to the fact that this section receives electrons from

only a tiny portion of the filament, at its very end. With increasing voltage, it receives current from an increasing portion, up to 1/5 of the filament at very high voltage (paths normal to cathode).

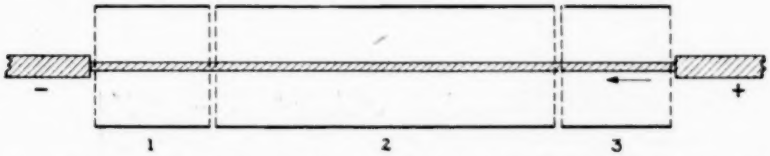

Fig. 9. Cross-section of special tube with anode divided in 3 sections. for testing reflection of electrons from the cathode.

The current to the middle section (curve II) begins at a voltage 200 volts lower than the theoretical critical value, and is nearly half an ampere at the critical voltage. From this point on it rises very rapidly.

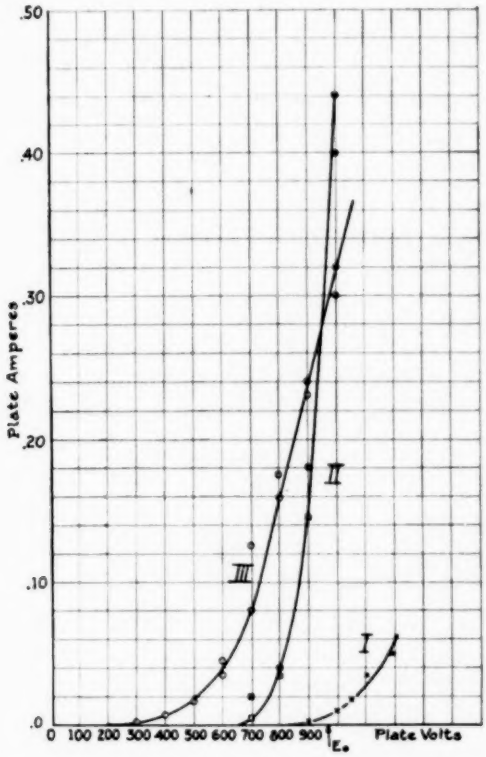

Fig. 10. Currents to three sections of anode shown in Fig. 9, as function of voltage.

This section receives primary electrons from approximately 3/5 of the filament, and in addition some electrons which have completed one path and have been reflected. Those electrons which retain at reflection

the full energy of their first flight, about 4 volts,[10] and emerge nearly parallel to the axis, should be able to reach the anode at 900 volts, according to Eq. (8). This leaves 150 milli-amperes to be accounted for by gas collisions—somewhat high, but possible, since the vacuum was not measured.

The current to section 3 begins at about 200 volts. This is too low to be accounted for by either gas collisions or reflection from the filament. It is accounted for, however, by reflection from the filament lead, which

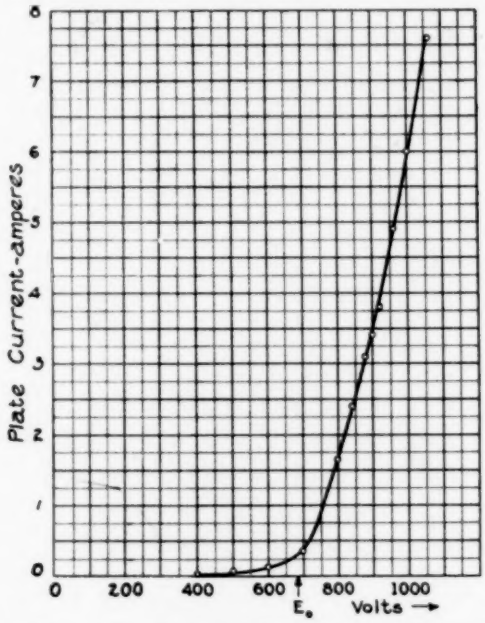

Fig. 11. Volt-ampere characteristic of tube with 2.5 mm filament and 2.5 cm diameter anode.

was a 3/8 inch diameter molybdenum rod, concentric with the filament. If the electrons impinging upon this rod were reflected, as they must be to a slight extent, they could reach the anode at 320 volts, according to Eq. (8), even if their initial energy at reflection were zero, and at 250 volts if their initial energy were 4 volts.

The shape of the characteristics in Fig. 5 and 10 is thus satisfactorily explained by reflection. It is quite possible, however, that there are other factors present, such as high frequency (Barkhausen) oscillations,[11] which have not been investigated.

[10] This is the voltage drop in the length of filament (15 cm) traversed in the first flight. The returning electron strikes the filament at a point 15 cm nearer the positive end than the point at which it left.

[11] Barkhausen and Kurz, Phys. Zeits. **21**, 1 (1920)

12. *Experiments with anodes of small diameter.* The effects of reflection may be made negligible by using tubes of small diameter, so that the paths are short. On the other hand, it is difficult to maintain the same relative degree of symmetry in small tubes. Fig. 11 shows the characteristic of a tube with a 2.5 mm diameter filament and a 2.5 cm diameter copper anode, water cooled.

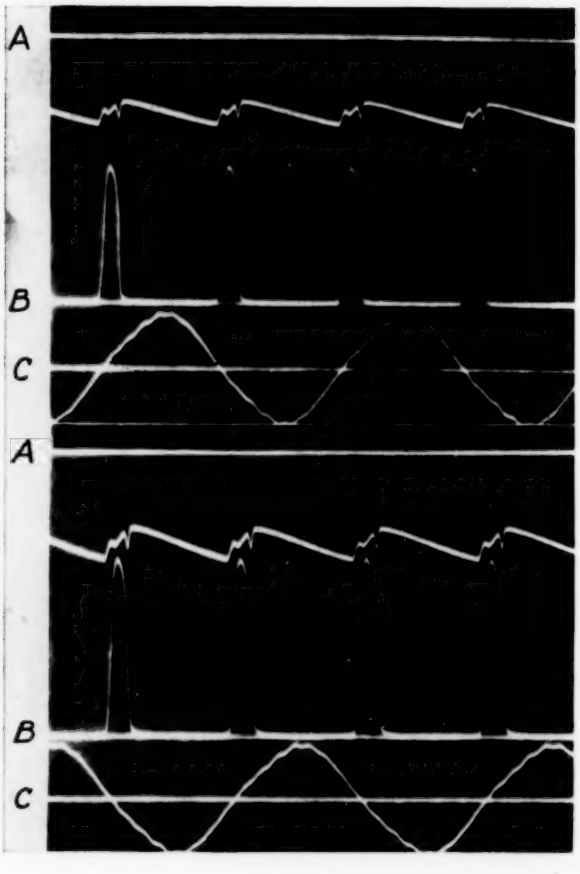

Fig. 12. Oscillogram showing plate current in a tube with 1 cm diameter tungsten cathode and 4.6 cm diameter anode, as function of instantaneous value of filament current. The lower curve C in each film is filament current, the middle curve B plate current, and the upper curve A plate voltage (deflection down).

The critical voltage is much lower than in Figs. 5 and 6, as predicted by Eq. (8) for smaller anode diameter, but is well defined, and the transition currents are not greater than are to be expected from the slight asymmetry and residual gas. The low alternating-current resistance of

only 35 ohms (the inverse slope of the curve at 1000 volts) is especially to be noted. This is about a hundred times smaller than the resistance of similar pliotrons at the same voltage, and is the main point of difference between magnetically and electrostatically controlled pure electron currents.

Fig. 13 shows the characteristic of a tube with a 2.5 cm diameter anode and a 1/2 cm diameter oxide-coated nickel cathode. In order to increase its mechanical strength at high temperature this cathode was supplied with a molybdenum core. The point to be noted is that the characteristic is considerably better than in Fig. 5, in spite of lack of uniformity in the spacing (only 4 mm) between anode and cathode.

13. *Experiments with larger filaments.* A series of tests with larger filaments is being carried out in this laboratory by Mr. J. H. Payne. Fig. 12 shows two typical oscillograms taken by Mr. Payne with one of these

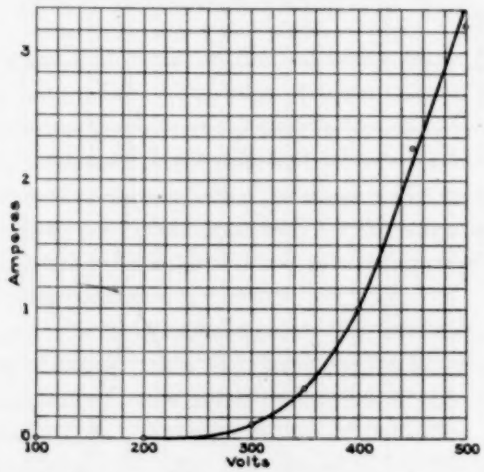

Fig. 13. Volt-ampere characteristic of tube with 2.5 cm diameter anode and 1/2 cm oxide-coated nickel filament.

tubes. The filament was a tungsten rod 1 cm in diameter and 56 cm long, the anode a copper tube of 4.6 cm internal diameter. The filament was heated with 60 cycle alternating current, and the anode potential maintained as nearly constant as possible.

In film 1 (above) the average potential was 1700 volts, which is recorded by the upper curve (base line A, deflection downwards). This potential was furnished by a 3000 volt d.c. generator, with a 50μf condenser across its terminals. The linear portions of the curve show the charging rate of this condenser, while the wavy portions are due to the rapid rate of discharge (36 amperes). The lower curve C gives the fila-

ment current (1600 amperes, 60 cycles) and the middle curve B the plate current. It is seen that the plate current is completely suppressed except during the short fraction of each cycle when the filament current is below a definite critical value. During these short periods, twice each cycle, it rises to 36 amperes (space-charge limit), and then falls abruptly to zero as the filament current again reaches the critical value.

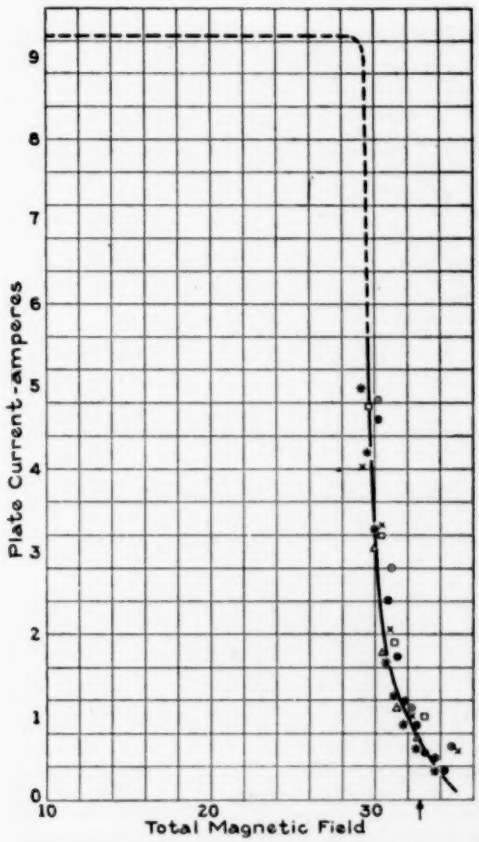

Fig. 14. Plate current-magnetic field plot of seven tests with combined radial and axial fields. Each test (denoted by a particular symbol in the plot) was made with a different proportion of axial field.

In film 2, below, the average anode potential was 3100 volts. Corresponding to this higher potential, the critical value of filament current was larger, so that the electron current flowed for a slightly longer fraction of each cycle, and attained the higher (space-charge limited) value of 45 amperes.

The values of critical filament current and voltage shown by these oscillograms agree completely with those predicted by Eq. (10).

14. *Tests of combined external and internal control.* It is predicted by Eq. (18), section 6, that under the combined influence of an externally impressed axial magnetic field, and an internally impressed circular field, the critical voltage should be the sum of the critical voltages that would be required for each of these fields separately. This prediction was tested over the whole range of combined fields from 100 per cent axial to 100 per cent circular field, and found to hold quite accurately. In Fig. 14 are plotted the results of 7 such tests for different field combinations from entirely axial to entirely circular field, for a tube with 2.5 cm diameter anode and 2.5 mm diameter tungsten filament. The anode potential was maintained constant at 1000 volts, and the total magnetic field varied by varying either filament current or solenoid current, or both. The effective magnetic field is taken, according to Eq. (16), as

$$\sqrt{[.0221\ H^2R^2+.0188(I-1.22\times10^{-7}\ w_0)^2]},$$

correction being made for the initial velocities w_0 in accordance with Maxwell's distribution law. The plot of plate current against effective magnetic field should give identical curves for all these tests. The experimental points obtained in the different tests are indicated by different symbols. It is seen that they fall on a common curve within experimental error. The fact that the cutoff occurs at a value slightly lower than the theoretical (indicated by the arrow) is due to imperfect centering of the filament in the small anode.

15. *Pring and Parker's experiments.* In 1912 Pring and Parker[3] reported a series of experiments with large carbon filaments, in which the current from the filament to a small metal disk decreased rapidly as the gas pressure was reduced, reaching values of the order of 10^{-12} amperes for moderate temperatures, and 10^{-9} amperes for the highest temperatures. The authors interpreted this as evidence that thermionic emission from carbon is due to chemical action between the carbon and gas, and would be zero in a perfect vacuum. O. W. Richardson,[1] defending the electron emission theory, suggested that the electrons might have been deflected by the magnetic field of the filament current, and showed that the filament current was of the right order of magnitude to prevent electrons reaching a symmetrical cylindrical anode of radius equal to the distance between disk and filament. Langmuir[12] suggested that the effect was due to electrostatic charges on the glass walls, and cited experiments in well exhausted lamps which showed exactly similar effects.

[12] Langmuir, Phys. Rev. 2, 484 (1913).

While the nature of thermionic emission is no longer in question, it seemed desirable to determine experimentally the relative importance of space charge and magnetic field in tubes of the type used by Pring and Parker (and by many previous investigators). This is easily accomplished by observing the current from filament to disk, first with the filament current flowing, and then with the filament circuit open but the filament still hot. A tube was constructed, as nearly as possible of the same dimensions as Pring and Parker's (see Fig. 15, copied from Dr. Pring's paper) but with a tungsten filament instead of carbon. This filament, 2.5 mm in diameter and 10 cm long, was mounted axially in a 17 cm bulb. The anode was a 1.2 cm disk of molybdenum, 7.25 cm from the filament. The distance from the disk to the glass wall was 1.5 cm.

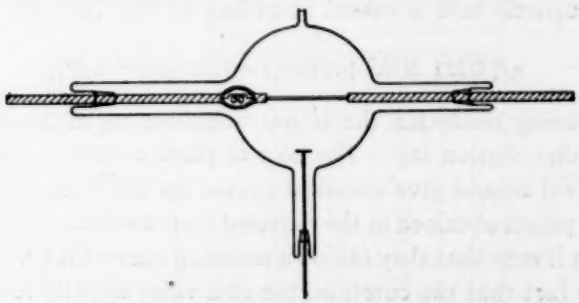

Fig. 15. Cross section of Pring's tube.

A current of 200 amp. heated the filament to 2500°K. This current was allowed to flow for 15 sec. (to give approximately constant temperature) and the plate current was read. The filament switch was then opened and the plate current again read, before the filament cooled appreciably. In order to make sure that there was no temperature limitation, the tests were repeated at 250, 300 and eventually 400 amp. At the latter temperature the time of heating was gradually increased until the filament melted at 4.5 seconds. At the lowest temperature the filament was capable of emitting 10 amp. and at the highest temperatures over 1000 amp.; *yet the current to the plate was less than 10^{-9} amperes, both with filament current flowing and not flowing.* The plate voltage was 250, and the vacuum good, of the order of 10^{-5} bars. It is evident that the smallness of the plate current was not due to lack of thermionic emission. It is also evident that under these conditions, which correspond closely to those used by Pring and Parker, it was not due to filament current, since the plate current was essentially zero even where no filament current was flowing.

The obvious explanation is charging up of the glass walls, as suggested by Langmuir. This was proved by the following experiment. A tungsten

wire was sealed through the glass wall of the tube just described and half imbedded in the inner surface so as to make contact with a thin coating of tungsten deposited by evaporation from the filament.[13] The walls could thus be charged to any desired potential, and the current from filament to plate measured for each potential. The results, given in Table IV, show (1) that the current to the disk decreased uniformly with increasing negative potential of the glass, and became zero in the absence of magnetic field at −21 volts. Electrons with initial velocities of 21 volts, though not to be expected from Maxwell's distribution law, are

TABLE IV

Current in Pring and Parker tube, as function of potential of glass.
Gas pressure 7 bars He; anode potential 250 volts.

Potential of glass	Current from filament to disk (1) with no filament current	(2) with 67 amp. filament current
0 volts	550 μamp.	8.0 μamp.
−3	475	5.0
−6	350	2.0
−9	225	.75
−12	50	.15
−15	4	.00
−18	0.2	.00
−21	0.00	.00

nearly always present in measurable quantity in 3 electrode tubes under similar conditions,[11] so that the absence of current in the previous experiment, and in the similar low gas pressure experiments of Pring and Parker, is fully accounted for by the potential of the glass. The limitation of the current is due to space-charge. The double function of gas ions (poor vacuum) in discharging the glass and annihilating space-charge, and so allowing more current to the disk, has been fully described by Langmuir.[12] (2) The results also show that when the glass is positive enough to allow current to flow to the disk, this current is greatly decreased by the magnetic field of the filament current. Further tests with the glass coating insulated, but with the disk much nearer (3.6 cm) to the filament, so that the shielding effect of the glass was less, gave 1 milliamp. to the disk at 250 volts with no filament current, and .075 milliamp. with filament current of 88 amp. Hence the magnetic effect suggested by Richardson is verified, though it must have been masked, under the conditions of

[13] To obtain contact it was necessary to reduce the oxide on the wire, which was accomplished by filling the bulb with low pressure hydrogen, and dissociating this by the hot filament. Atomic hydrogen reduces WO_3 at room temperature.

Pring and Parker's experiments, by the much greater effect of space-charge.

I gratefully acknowledge the able assistance of Mr. F. R. Elder in the experimental part of this work.

RESEARCH LABORATORY,
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January 14, 1925

ELECTRON EMISSION FROM OXIDE COATED FILAMENTS

By Lewis R. Koller

Abstract

Emission from oxide coated filaments.—(1) *Effect of various gases.* Platinum iridium filaments were coated with oxides of Ba and Sr by repeatedly dipping in a solution of the nitrates and burning in a CO_2 atmosphere. Under good vacuum conditions the emission corresponds to the equation $I = aT^2e^{-b/T}$ where $a = .00107$ amp/cm^2 and $b = 12{,}100$ deg. for the filaments studied. The presence of oxygen in small amounts (10^{-3} mm) decreases the emission ten to a thousand fold, depending on the temperature, while argon, hydrogen, CO and CO_2 cause a great increase. These results indicate that the emission is due not to the oxides but to a film of metal. (2) *Positive ion bombardment* also increases the emission, probably by reducing some of the oxide. (3) *Flashing at 1600°K* for 1 to 5 min. de-activates the filament, but heating at lower temperatures (900°K) restores the activity. (4) *Distribution of initial velocities* was found to follow Maxwell's law, but the average energy came nearly 30 per cent higher than that corresponding to the temperature of the filament.

ELECTRON emission from the oxides of the alkali earths was first studied by Wehnelt in 1904. He found that a small amount of CaO on platinum gave a very high emission and this type of cathode has since been known as the Wehnelt cathode. Subsequently, the emission from such cathodes was studied by Richardson and in more recent years by Arnold, Davisson and Germer, Wilson and others.[1]

Some irregularities observed by the writer in the behavior of Wehnelt cathodes led to an investigation of the effects on them of various gases. It was found that under high vacuum conditions very uniform results are obtained, while very small traces of gas may produce considerable changes in emission.

The filaments used consisted of a platinum iridium core (10 to 15 percent iridium) 9 mils (.22 mm) wide by 0.25 mil (.006 mm) thick on which was deposited a coating of the oxides. The method of applying the coating was to dip the wire into a solution containing respectively three percent of barium nitrate and two percent of strontium nitrate and then burn it for a few seconds at a high temperature in an atmosphere

[1] W. Wilson, Phys. Rev. **10**, 79 (1917);
C. Davisson and H. A. Pidgeon, Phys. Rev. **15**, 553 (1920);
H. D. Arnold, Phys. Rev. **16**, 70 (1920);
Davisson and Germer, Phys. Rev. **15**, 330 (1920).

of carbon dioxide. This process was then repeated until the coating reached the desired thickness. About 40 cycles were usually sufficient.

Such a coating consists largely of the carbonates, as can readily be demonstrated by dipping a filament in hydrochloric acid, which results in a rapid evolution of gas. This evolution of gas takes place even after a filament has been burned for several hundred hours.

The filaments were mounted in tubes with cylindrical nickel anodes and given a condensation pump exhaust. During exhaust the bulb was baked out for at least an hour at 360°C. The anode was then heated by high frequency induction to drive out occluded gases, and the filament was flashed at 1350°K for 15 minutes. The tube was then immersed in liquid air and measurements made while the pump was running. (In some cases instead of a nickel anode a film of tungsten was deposited on the walls of the bulb by the evaporation of a tungsten filament and this was used as an anode.) Measurements of emission were then made at various filament temperatures.

Effects of Gases

When the values of log (i/T^2) are plotted against $1/T$, a straight line results (as in Fig. 1) showing that the emission obeys the equation $i = aT^2e^{-b/T}$. The constants determined from this line are

$$a = 1.07 \times 10^{-3} \text{ amp. per sq. cm}; \quad b_o = 12{,}100 \text{ deg.}$$

Temperatures were found from the relation between temperature and resistance determined for an uncoated strip by Dr. H. A. Jones of the Research Laboratory at Schenectady.

If a small pressure of oxygen (5×10^{-3} mm) is now introduced into the tube and the values of i/T^2 are again measured and plotted against $1/T$ a curve such as the lower one of Fig. 1 results. The emission still obeys the same law as before but the constants a and b have both increased to the values

$$a = 4.27 \times 10^3; \qquad b = 35{,}900.$$

While a has increased over 100,000 fold, the increase in emission due to the increase in a is more than counterbalanced by the decrease in emission due to the increase in b so that the emission of the filament in oxygen is less than that in vacuum. It can be seen from the figure that at high temperatures the curves would cross and the emission in the presence of oxygen would be higher than in vacuum. At these temperatures however, the rate of evaporation of the oxides is so high that the filaments cannot be operated.

On pumping out the oxygen the slope of the curve remains unchanged while the value of a increases slightly until pressures of the order of 10^{-4}

mm are reached. Below this pressure the changes are rather erratic, but by pumping and burning the filament at normal operating temperature, it can be restored to its initial condition. Unless the last traces of oxygen are pumped out, no heat treatment alone can restore the emission.

If a filament is burned at sufficiently high temperatures to evaporate the oxides and determinations of a and b_o are made at frequent intervals, it is found that the values tend to pass from those observed in vacuum to those observed in oxygen.

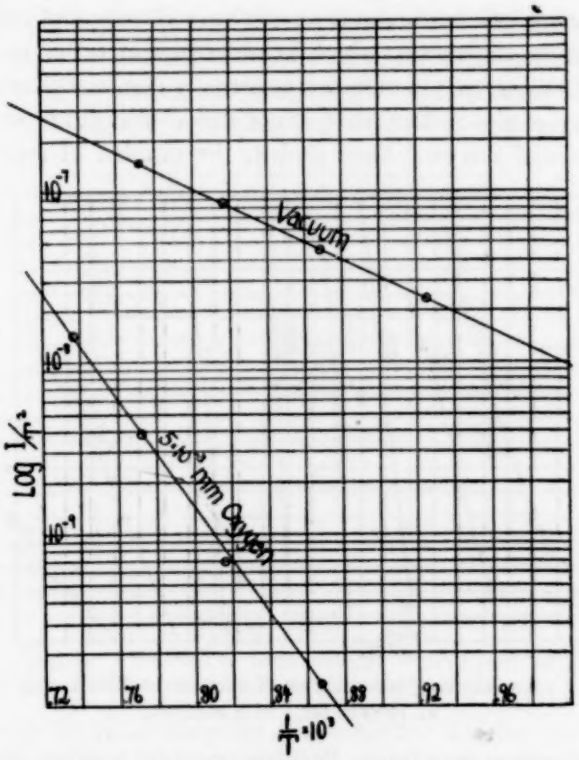

Fig. 1. Log (i/T^2) as a function of $10^3/T$.

The foregoing results indicate that the emission is due, not to the oxides, but to a film of metal, and anything which tends to destroy this film either by evaporation or by oxidation destroys the emission.

Water vapor has the same effect as oxygen in "poisoning" the emission. In the presence of gases such as argon, carbon dioxide, carbon monoxide or hydrogen, the emission is increased by a factor of from 10 to 100 depending upon the history of the filament. This increase is due to an increase in a while b_o remains practically constant. Conditions in these

gases are difficult to reproduce and reliable quantitative data have not been obtained.

Effects of Positive Ion Bombardment

It is found that when a filament is operated under conditions such that positive ion bombardment can take place, that is, with a small amount of residual gas present and an anode voltage greater than the ionizing voltage, the emission is always greatly increased. The increase may become permanent and remain even after the gas has been removed. The positive ion bombardment seems to have the effect of reducing some of the oxide to the metal, which is necessary in order to get a high emission. This increase in emission is actually due to a change produced in the nature of the surface, and is not due to secondary emission, for, as Davisson and Germer[1] have shown, the number of secondaries per

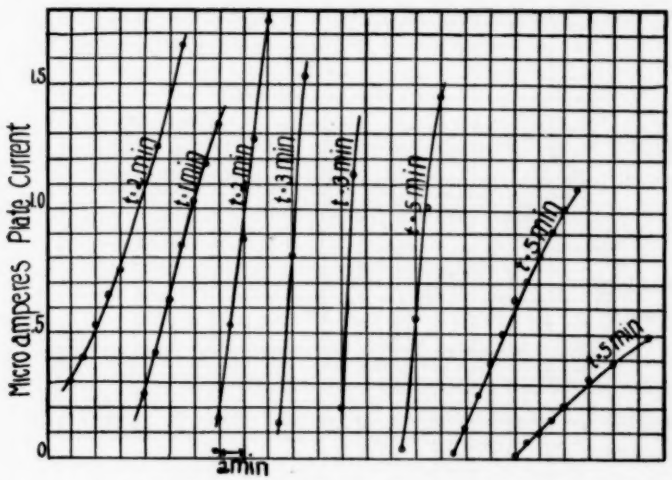

Fig. 2. Curves showing re-activation of filament at 900°K after burning at 1600°K for 1 to 5 minutes.

positive ion is never very large. Bombardment by positive ions, however, can change the nature of the surface from one having a low primary emission to one having a high primary emission. For example, a filament which gave a saturation emission of 1.9 milli-amp. in a good vacuum gave an emission of over 20 milli-amp. at a pressure of 0.5×10^{-3} mm of carbon dioxide.

Effects Due to Temperature

While the active material may be produced in part by positive ion bombardment it is also produced by the effect of the temperature at which the filament is operated. This is shown by the curves of Fig. 2.

The filament was partially de-activated by burning at 1600°K for a short interval. The temperature was then dropped to 900°K and the rate of re-activation measured. The values of emission were then plotted against time as shown in the figure. A series of such activation curves was taken for various periods of flashing at the high temperature. From the figure it can be seen that the rate of activation increases with the time of flashing at the high temperature, passes through a maximum and then decreases. The explanation is that "active" material is formed at the high temperature but the rate of evaporation is too high to permit it to remain on the surface. At lower temperatures the surface becomes partially covered by some of the material which diffuses from inside the oxide coating. The rate at which the surface becomes covered depends on the concentration within the coating. This increases with the length

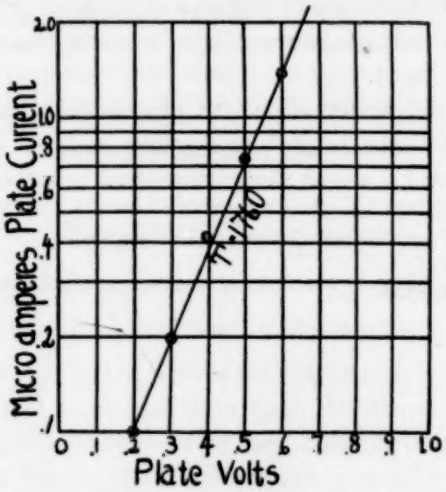

Fig. 3. Log i as a function of plate voltage, showing that distribution of initial velocities of electrons is Maxwellian.

of time of flashing up to the point where further flashing results in more "active" material being lost by evaporation than is formed. This is analogous to the phenomena observed in the case of thoriated filaments, which have been described by Dr. I. Langmuir.[2] In the case of oxide coated filaments, however, sufficient active material may be present initially so that it is not necessary to use the temperature treatment.

Initial Velocities

Measurements of initial velocity of the emitted electrons were made to see whether the velocity distribution followed Maxwell's distribution

[2] Langmuir, Phys. Rev. 22, p. 357, 1923.

law. The procedure used consisted in measuring the space current with low retarding and accelerating voltages on the plate. The values of log i when plotted against V gave a straight line as shown in Fig. 3, showing that the distribution obeys Maxwell's law. The average value of the kinetic energy of the emitted electrons calculated from this curve corresponds to 1760°K which is somewhat above the temperature of the filament (1368°K). In the presence of hydrogen, this current-voltage line is shifted towards lower voltages and in the presence of oxygen, towards higher voltages.

Since writing this paper, the article by Davisson and Germer has appeared.[3] Many of the phenomena which they describe agree with those observed by the writer. Their value for the work function is higher than that found by the writer for good vacuum, but this difference may be within the limits of variation of this type of filament or the filament may have been in a condition intermediate between those represented by the two curves of Fig. 1.

In conclusion the writer wishes to express his thanks to Dr. Saul Dushman for his many helpful suggestions and his constant interest and encouragement.

RESEARCH DIVISION,
EDISON LAMP WORKS OF THE GENERAL ELECTRIC CO.,
HARRISON, N. J.
January 9, 1925

[3] Davisson and Germer, Phys. Rev. 24, 666 (1924)

THE SPECIFIC HEAT OF INCANDESCENT TUNGSTEN BY AN IMPROVED METHOD

By Lester I. Bockstahler

Abstract

Specific heat of a tungsten filament at 2425°K.—A modification of a method suggested by Smith and Bigler[1] is used, in which the uncertain cooling effects at the ends of the filament are eliminated. A tungsten filament surrounded by a cylindrical anode is heated to incandescence in vacuum by a 60 cycle current. By means of a double strip oscillograph continuous photographic records of the heating-current and of the thermionic current variations are obtained. Since saturation potentials are applied to the anode at all times, the small changes in thermionic current are taken as proportional to the temperature changes. Knowing the magnitude of the temperature changes and the mean power dissipated in the filament, its specific heat is calculated from the theoretical relations deduced by Corbino. The temperature of the filament is determined with a pyrometer for a steady current giving the same thermionic emission as the alternating current under consideration. This temperature is taken to correspond to the mean thermionic current as indicated by a d.c. ammeter. The specific heat of tungsten found by this method is 0.045 for temperatures between 2375 and 2475°K, in good agreement with previous determinations.

Method of making tungsten seals in Pyrex is described.

Historical Survey

CRANZ[2] has shown that when a thin filament is heated by an alternating current of sinusoidal wave form the temperature variations are likewise sinusoidal and have twice the frequency of the heating current. H. Ebeling[3] by means of an oscillograph was able to verify the conclusions of Cranz. Some of the assumptions made by Ebeling appeared untenable to O. M. Corbino[4] so he took up the problem. His theory is used in the present method of specific heat determinations and will be given later.

By means of a Braun tube oscillograph, Corbino found that the temperature variations lagged very nearly 90° with respect to the power input. Using a Wheatstone bridge arrangement[5] in conjunction with a ballistic galvanometer, he observed the resistance and current changes

[1] Smith and Bigler, Phys. Rev. **19**, 268 (1922)
[2] Cranz, Zeits. f. Math. und Phys. **34**, 92 (1889)
[3] H. Ebel ng, Ann. der Phys. **27**, 391 (1908)
[4] O. M. Corbino, Phys. Zeits. **11**, 413 (1910)
[5] Corbino, Phys. Zeits. **13**, 375 (1912)

in a tungsten filament when a ballast resistance was switched in and out of the lamp circuit in which a direct e.m.f. was operative. From these data and the temperature coefficient of resistance, he calculated the specific heat of the filament.

Worthing[6] has obtained values of the specific heat of tungsten for temperatures between 1200°K and 2400°K. His method depended on reading the instantaneous filament current and the voltage drop at any desired time after the steady heating current had been changed a small amount.

Gaehr[7] modified Worthing's method by using a system of motor driven switches to vary the resistances of the lamp current in cycles, thereby more nearly approaching steady state conditions.

Hunkel[8] mounted a rotating contact switch on the shaft of an a.c. generator and measured instantaneous values of heating current, voltage, and electron emission for tungsten filaments of different diameters. Temperatures were found by aid of Richardson's thermionic current equation. The heat capacity of the filaments was found to be independent of the heating current frequency.

THEORY

If one considers a filament heated in vacuum, the heat loss by convection is negligible, the heat capacity of the filament itself must be taken into account, and due regard must be given to the change in resistance during the cycle. The exact law of variation with temperature of the radiation of energy may be left undetermined.

Let $e_0 \sin \omega t$ = impressed electromotive force;
T = instantaneous temperature;
T_m = mean temperature during the cycle;
$f(T)$ = rate of radiation of energy at temperature T;
c = heat capacity of filament;
r_m = mean filament resistance at T_m;
a = temperature coefficient of resistance within the limits of temperature oscillation;
θ = temperature above or below T_m at any instant;
t = time;
$\omega = 2\pi$ times the frequency of heating current.

[6] Worthing, Phys. Rev. **12**, 199 (1918)
[7] Gaehr, Phys. Rev. **12**, 396 (1918)
[8] Hunkel, Phys. Zeits. **12**, 252 (1923)

Equating the rate at which energy is supplied to the filament to the rate at which it is emitted and stored in the filament,

$$\frac{e_0^2 \sin^2 \omega t}{r_m(1+a\theta)} = f(T_m+\theta)+c\frac{d}{dt}(T_m+\theta)\,. \tag{1}$$

If $f(T_m+\theta)$ is now expanded into a Taylor's series and the second and higher power terms in θ neglected, the equation becomes

$$\frac{e_0^2 \sin^2 \omega t}{r_m(1+a\theta)} = f(T_m)+\theta f'(T_m)+c\frac{d\theta}{dt}\,. \tag{2}$$

Neglecting higher powers of θ and expanding $\sin^2 \omega t$

$$(e_0^2/2r_m)(1-\cos 2\omega t) = f(T_m)+a\,\theta f(T_m)+\theta f'(T_m)+cd\,\theta/dt. \tag{3}$$

The average power dissipated in the wire is

$$e_0^2/2r_m = f(T_m) = W. \tag{4}$$

Let

$$Q = af(T_m)+f'(T_m). \tag{5}$$

Equation (3) then reduces to

$$c\;d\,\theta/dt+Q\,\theta = -(e_0^2/2r_m)\cos\;2\omega t. \tag{6}$$

A solution of this linear differential equation shows

$$\theta = \Theta\,\cos(2\omega t-\varphi), \tag{7}$$

where

$$\Theta = -(e_0^2/2r_m)\cos\varphi/Q, \tag{8}$$

and

$$\tan\varphi = 2c\omega/Q. \tag{9}$$

The temperature oscillations have twice the frequency of the impressed e.m.f. and lag behind the power input by an angle φ.

An expression for the heat capacity of the filament follows by eliminating Q from Eqs. (8) and (9)

$$c = -(W/2\omega\Theta)\sin\varphi \qquad \text{(joules/deg)}$$

The specific heat is found by dividing both members of this equation by the mass of the filament.

The experimental method used to measure Θ and φ has already been briefly described.[9] If a filament, heated by a.c., and an anode, with saturation potential applied, are placed in a vacuum, it may be assumed, because of the high mobility of the electron, that the thermionic current will closely follow the temperature changes of the filament. By means of a double-strip oscillograph, one may obtain a continuous photographic record of the impressed e.m.f. and the thermionic current variations. The amplitudes of the latter may be translated into amplitudes of

[9] Smith and Bockstahler, Proc. Nat. Acad. Sci. 10, 386 (1924)

temperature variations, when the temperature corresponding to the mean thermionic current is known.

Construction of Filaments and Lamps

The filaments, Fig. 1, were made from pure tungsten wire, obtained from the General Electric laboratories. The thermionic current was collected from the uniformly heated central portion *cc*. A fine tungsten wire *p*, tied 2 cm from the end of the filament, served as a potential lead. The tungsten wires were fused to pieces of copper wire *b* which were in turn fused to tungsten rods *d*. These were sealed through the glass. A helical molybdenum spring *s* kept the filament taut.

Fig. 1. Filament mounting and connections.

The lamps were made of Pyrex glass tubes 3.2 cm in diameter and about 25 cm long. Fig. 2 shows a sketch without the filament, which was placed axially in the tube. The cylindrical anode *a* which collected the electron emission from the central portion of the filament, was pierced by two diametrically opposite holes *f*, 1 cm in diameter. These allowed clear vision of the filament. Two guard rings *e*, 2.5 cm long, were provided to prevent the electrons from the non-uniformly heated ends of the filament from reaching the anode. Rings and anode were made of molybdenum.

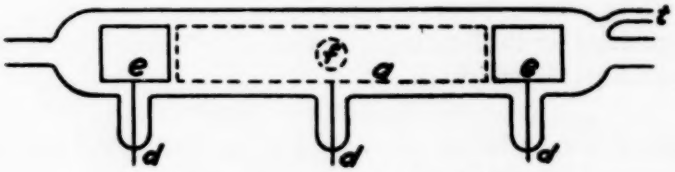

Fig. 2. Diagram of lamp without filament.

Tungsten-Pyrex seals were made as follows. A piece of the tungsten rod, 4 or 5 cm long, and 0.075 cm in diameter, is heated to a dull red heat in a gas-oxygen flame and is then drawn across a stick of potassium nitrite. The tungsten looks bright and clean after it is washed under the tap. Then a piece of Pyrex tubing is drawn out until it is just large enough to slip over the rod. The rod is passed through the flame until it assumes a bright bluish color. A short piece of the drawn out Pyrex tube is then placed on the rod and the whole heated until the glass and tungsten are both a bright red color. On cooling, a golden colored flux

should appear between the glass and the tungsten. The rod with its glass sheath is now sealed into a tube by drawing the tube down to a convenient size and placing the rod in position, then heating the tube and pressing the glass firmly upon the tungsten with a pair of heavy tweezers. Usually the seal must be heated and squeezed several times. In this way a clean, tight joint may be obtained.

The lamps were out-gassed by the usual methods of baking and the use of liquid air. The exhaustion was carried out by means of a mercury vapor pump backed by a Gaede mercury and an oil pump. Before sealing a lamp off the filament was aged for ten hours at a temperature about 200° above that used in the final observations. During this time, a positive potential 25 per cent in excess of that used in the experiment, was applied to the anode and guard rings. Application of liquid air and pumping was continued during the ageing. The pressure during this period, as indicated by a McLeod gauge, was less than 10^{-5} mm of mercury.

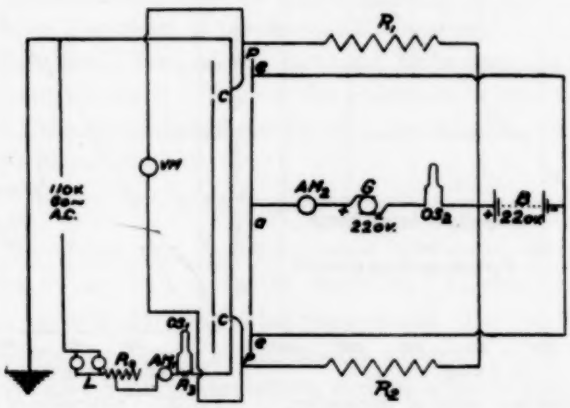

Fig. 3. The circuit used.

The Circuit

Fig. 3 shows the circuit used in making the observations; c, p, a, e refer to the parts of the lamp as indicated above; os_1 and os_2 are the strips of a Duddell high frequency oscillograph. A symmetrical return of the thermionic current is provided by the resistances R_1 and R_2, each of the order of 1000 ohms. The heating current was controlled by two carbon lamps L and a slide wire rheostat R_0. Observations consisted in reading simultaneously the heating current AM_1, the voltage drop in the filament VM, and the thermionic current AM_2, at the instant the photographic plate was dropped in the oscillograph.

Temperature Determinations

Temperatures were found by means of a disappearing-filament pyrometer, the parts of which were mounted on movable carriages on a solid track of channel iron, three meters long. The objective was an achromatic lens of 30 cm focal length and 5 cm diameter. A piece of glass with wave-length transmission of 0.665μ was placed in the eye piece of the observing telescope. The system had a magnification of five. Appropriate diaphrams and a blue glass absorbing screen were placed directly in front of the pyrometer lamp.

A single filament lamp, similar to the one previously described, was constructed without an anode. Pure tungsten wire for this filament was obtained through the kindness of Dr. Dushman. It was part of the lot he had used in his work on thermionics and for which he had obtained

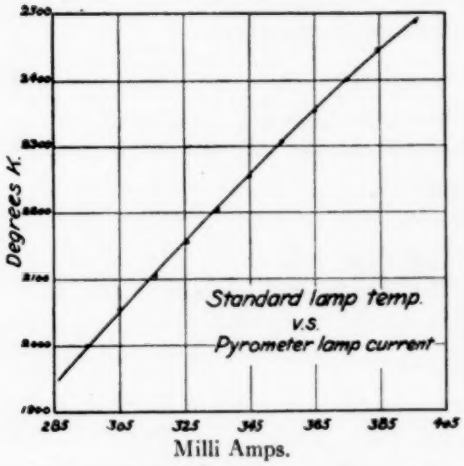

Fig. 4. Calibration curve of pyrometer.

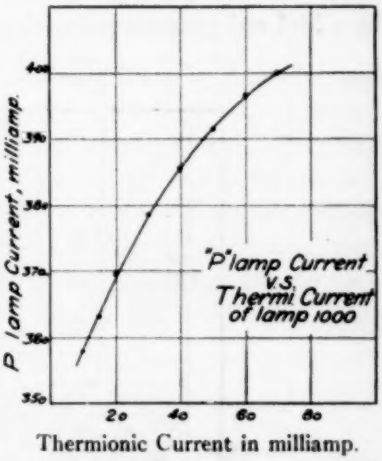

Fig. 5. Calibration of experimental lamp in terms of pyrometer current.

accurate calibration curves of the temperature as a function of the heating current. After ageing this lamp for 15 hours at about 2500°K, it was taken to the Nela Laboratories at Cleveland, and a series of heating-current-temperature determinations were made by Dr. Forsythe using his pyrometer. A careful plot of these values was made. Taking this lamp as a standard, the pyrometer lamp was calibrated in the usual manner and the curve of Fig. 4 constructed. The experimental lamp was now substituted for the standard lamp (all other parts of the pyrometer remaining unchanged). Fig. 5 shows the pyrometer lamp current plotted against the thermionic current of the experimental lamp for various brightness matches of the two lamps. By means of the two curves the temperature of the experimental lamp was determined.

It was found that, when the experimental filament was heated by an alternating current, small vibrations of the filament, probably due to electromagnetic action, prevented accurate matching. Consequently, temperatures were determined with a direct heating current for a series of values of thermionic current. Equal values of mean thermionic current were taken as indicating equal mean filament temperatures for either direct or alternating heating current.

Temperatures so obtained were in good agreement with those calculated from Worthing's[10] published results on the radiation from tungsten filaments at various temperatures.

Errors and Corrections

The observed value of the heating-current was corrected for the current passing through the voltmeter and the resistances R_1 and R_3. The cooling effect of the electronic emission and the effect of reflected radiation is automatically cared for by the term $f(T)$ in Eq. (1).

Following the argument of Cooke and Richardson,[11] it may be shown that the disturbing effect of the returned thermionic current on the heating current is small. If r is the resistance, i the direct heating current, and c the mean thermionic current, the maximum instantaneous heating of the filament is

$$H = r(i^2/2 + c^2/12) .$$

In case of an alternating heating-current the mean disturbance will be less, since in one half cycle the thermionic current assists, and in the next half cycle it opposes the heating current. The fact that, because of the non-linear variation of thermionic emission with temperature, a filament will give a larger thermionic current when heated by a.c. than when heated by an equal d.c., causes a slight error in the absolute value of the temperatures determined. This error is not carried into the calculations, since only temperature differences are considered.

Measurements Made from Plates

Fig. 6 is a reproduction of a tracing made from one of the plates. The maximum and minimum points of the curves were indicated by pricking the emulsion with a needle. Each point was numbered and rectangular coordinates determined for it. The mean displacement of the thermionic current wave form was taken as corresponding to the mean value of thermionic current and to the temperature corresponding to that current.

[10] Worthing, Phys. Rev. **10**, 393 (1917)
[11] Cooke and Richardson, Phil. Mag. **25**, 630 (1913)

The value of the temperature oscillations was obtained on the assumption that temperature-changes are proportional to the changes in thermionic current.

From the coordinates of the points at which the heating and thermionic current oscillations pass through their zero values, the phase-difference between the power-input and the temperature-variations was found. The lengths of the two curves compared were taken, as nearly as possible, from one and the same time-interval on the plate; thus, the effects of the acceleration of the falling plate were practically eliminated.

Fig. 6. Tracing of record obtained with a double-strip oscillograph, showing phase displacement of heating current and temperature of the filament.

Data and Results

The length of the central portion of the filament was 11.5 cm, the diameter 0.0038 cm, the mass 0.00248 gm, and its resistance (cold) 8.05 ohms.

Plate No.	Heating cur. (amp.)	Power input (watts)	Mean T. C. (milliamp.)	Ampl. of T. C. (milliamp.)	Mean temp.	θ	φ (mean)	Sp. heat
1022	.3192	7.581	19.9	4.33	2371°K	21.5°	88.0	0.045
1010	.3201	7.618	20.0	4.85	2372	22.5	91.2	.044
1016	.3201	7.634	20.0	4.61	2371	22.0	94.0	.044
1004	.3290	8.291	29.8	6.78	2411	24.0	90.0	.044
1020	.3287	8.257	30.0	6.93	2412	24.0	89.6	.044
1026	.3292	8.296	30.5	7.17	2414	25.0	88.7	.043
1023	.3357	8.788	39.8	9.59	2442	26.5	88.9	.043
1005	.3368	8.841	40.0	9.18	2442	26.0	90.4	.044
1017	.3371	8.798	40.5	9.68	2444	27.0	89.6	.042
1006	.3433	9.303	50.0	11.75	2467	25.5	90.4	.047
1021	.3423	9.259	50.0	12.11	2467	26.0	89.6	.046
1027	.3427	9.287	50.5	12.18	2469	26.0	87.6	.046
1029	.3457	9.489	54.5	13.34	2477	26.5	87.7	.046
1030	.3459	9.478	55.0	13.60	2478	26.5	89.2	.046
1018	.3501	9.715	60.5	14.76	2486	26.5	89.7	.047

Conclusions

(1) This method is practicable for determining the specific heat of a substance in filament form at temperatures of incandescence.

(2) The specific heat of tungsten between the temperatures of 2375° and 2475°K has a mean value of 0.045. These values are in good agreement with those found by Worthing and Gaehr. Their value of specific heat is 0.046 for temperatures of 2400°K and 2500°K. The value found by Corbino at about 2100°K was 0.0425.

(3) The temperature lags very nearly 90° with respect to the power input. This agrees with the observations of Corbino and Hunkel.

(4) A modification in the sensibility of the oscillograph and in the size of the filament used will permit a larger range of temperatures to be covered.

The writer is under obligations to Dr. Saul Dushman who kindly furnished the tungsten wire and to Dr. W. E. Forsythe who supplied important data concerning the pyrometer filament. The writer also desires to express his thanks to Professor K. K. Smith for suggesting the problem, and to Mr. Küng, the instrument maker, for his untiring interest and assistance in the work.

NORTHWESTERN UNIVERSITY,
EVANSTON, ILLINOIS.
May, 1924.*

* Received Nov. 29, 1924—Ed.

STANDING ELECTRIC WAVES ON PARALLEL WIRES

By W. S. Huxford

Abstract

Measurement of short electric wave-length with a parallel wire receiving system.—Electromagnetic waves of from one to ten meters in length and highly constant in nature were obtained by means of a valve oscillator. Two types of generating circuits are described. Analysis of the possible free modes of electric vibration of the parallel wire receiving system indicates that for normal coupling with the valve generator there are always to be found two sets of current maxima. When the sliding bridge is at a position indicating maximum current flowing through the thermo-junction, standing waves exist in a section of the parallel wires included between the bridge and one or other end of the wire system. A change in the terminal conditions at either end of the parallel wires changes the position of the set of resonance points formed by reflection of waves from that end, but does not alter the location of current maxima which are determined by standing waves reflected from the other end. The half wave-length is equal to the distance between successive positions of the bridge at resonance in each of the two sets. Measurements obtained were constant to one part in one thousand for readings requiring a total time of only from two to four minutes. The measured wave-length is independent of mutual effects of exciter and receiver. It is not altered by a change in the diameter or spacing of the receiving wires, or by a change in the material, provided it is non-magnetic.

THE method of measuring wave-lengths by means of two parallel wires upon which standing electric waves are maintained has been in use for some time. The arrangement of bridged wires is usually spoken of as a Lecher system. In the course of a series of experiments with short waves it became necessary to measure accurately each wave-length in a short time. No method was available for determining with rapidity and precision those positions of the bridge at resonance between which the half wave-length is to be measured. The following note aims to give compete information as to the possible modes of vibration of the simple parallel wire system when used as an isolated receiver of undamped oscillations.

Oscillation Generators

Two very similar triode-valve generating circuits were employed, the essential parts of which are shown in Figs. 1A and 2B. The valve used was a modified form of the Radiatron UV-202 in which the grid connection is fused through the top of the glass tube, so that the usual electrostatic coupling between grid, plate and filament leads is reduced. Non-

metallic sockets were used, and every precaution was taken to secure a minimum of capacity and a symmetrical arrangement in the circuits.

In the first circuit (Fig. 1A), two horizontal brass tubes, 5 mm in diameter, are soldered to the plate and grid leads and are mounted in a vertical plane parallel with each other at a distance apart of 3 cm. Two brass rods fit into these tubes to form a telescoping system, easily variable in length. The condenser *C* consists of two brass plates, each 5 cm square, adjustable as to spacing and as to position along the rods. The plate potential employed is 210 volts, and with normal filament heating the plate current is from 30 to 40 milliamp. When the oscillations start, this current suddenly increases to nearly double its original value. The range of wave-lengths with this set, employing rods and tubes 20 cm in length, is from 100 to 300 cm.

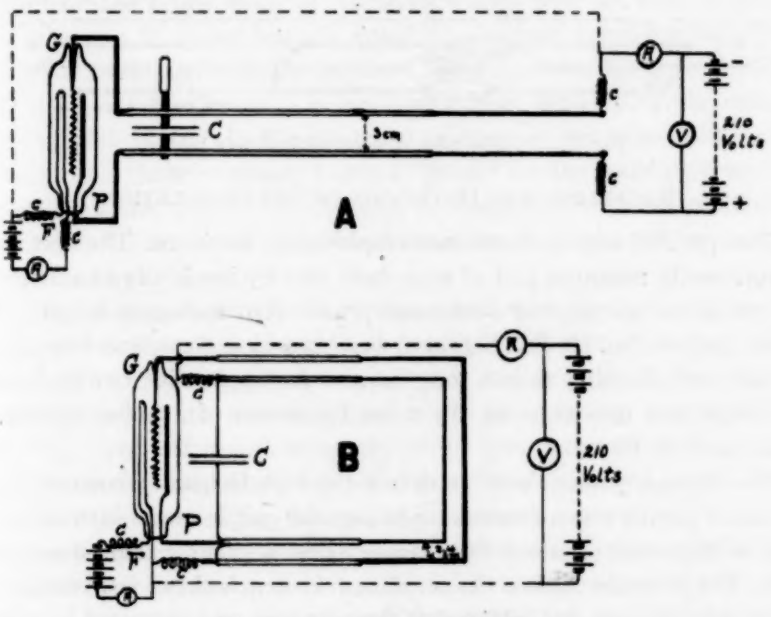

Fig. 1. Generating circuits used.

An alternative generator is shown in Fig. 1B. As in the circuit described above, grid and plate loops consist of tubes and sliding rods. Here the arrangement is more compact, and a condition of stable oscillation more easily secured. This circuit is similar to one employed by Dunmore and Engle[1] for generating waves from 9 to 16 meters in length. The brass condenser plates *C* are 2.4 cm square and are adjustable for spacing but fixed in position. The square shaped loops determine vertical planes,

[1] Dunmore and Engle, Inst. Radio Eng., Oct. 1923.

which are 2.4 cm apart. The values for plate potential and plate current are as indicated for the first circuit. The range of wave-lengths obtained with this generator is 200 to 1000 cm.

Choke coils, consisting of 20 to 30 turns of No. 18 insulated copper wire wound on soft iron cores .6 cm in diameter, are placed in the circuits at the points marked *c*. These serve to keep the high frequency currents from battery and control leads, and confine them to the oscillatory circuits indicated by the heavier lines in the figures. With careful adjustment the circuits oscillate readily, the wave-length usually remaining constant to within a millimeter. Both generators were mounted on the same control panel and this could be moved to any desired position with reference to the parallel receiving wires.

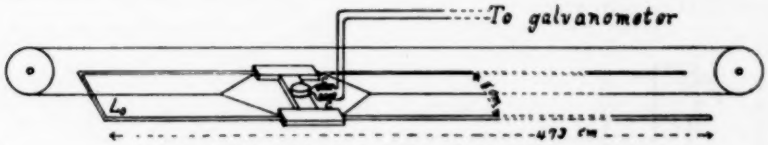

Fig. 2. Parallel wire receiver with sliding bridge.

Reception and Detection of the Oscillations

Two parallel wire systems were employed as receivers. The first was a permanently mounted pair of wires held taut by insulators at a height of 80 cm above one edge of a laboratory table four meters in length. The wires (copper No. 12, B & S gauge) were spaced at 8 cm, and were joined at one end, forming thus a long narrow rectangle with one end open. A bridge was moved along the wires by means of a pulley system as illustrated in Fig. 2.

The thermo-element used to detect the high-frequency current in the resonant circuit was a constantan-manganin couple made with wires .05 mm in diameter, obtained from larger wires by etching them down with acid. The junction used on the permanent system had two such wires each 1 cm long, crossed and soldered at their centers, and mounted in a brass case which was carried on a sliding bridge grooved to follow along the wires. Contact was maintained by terminal leads, one from the constantan end, one from the manganin end, each of which rubbed upon one of the two parallel wires. The other unlike ends of the thermal pair were joined by long leads (Fig. 2) to a Leeds and Northrup galvanometer having a resistance of 26 ohms and a sensitivity of 10^{-9} amp. per scale division.

When the generating circuit was set in operation at a distance of 50 to 150 cm from the parallel receiving wires, slight indications of current

could usually be noted on the galvanometer for any position of the bridge. As the bridge was moved along the wires there were certain well defined points at which the thermo-junction current rose suddenly to very high values. These positions of the bridge, or resonance points, could be determined with great accuracy. A slow motion pulley with crank enabled the operator to check each observed position many times. It is with the factors which determine the location of these positions of the bridge at resonance that the present paper is concerned.

Modes of Oscillation of Parallel Wires

Experiment shows that the possible modes of free electrical vibration of an isolated linear conductor are analogous to the possible modes of mechanical vibration of a stretched elastic string. In each case the fundamental or prime mode of vibration is such that the total length of wire or string is approximately equal to the half wave-length of the oscillation associated with the system. In both instances the frequencies of all the free vibrations of a given system bear (nearly) simple integral ratios to each other. In the electrical problem it has been shown conclusively that the wire merely forms a "guide" for the standing electrical waves when the system is vibrating in resonance with an oscillating electrical field, and that the disturbance travels along the wires with the speed of light in air.

Earlier investigators who were concerned with the analysis of the free modes of electrical vibration of parallel wires met with many difficulties. The employment of a spark gap and several closely coupled circuits gave rise to a complicated series of standing waves on the receiving wires. It is not necessary to go into detail concerning these earlier investigations, however, since many undetermined factors have since been eliminated by the use of undamped waves. J. S. Townsend[2] has attacked the problem, using a Lecher wire system coupled to a valve generator by means of a loop. A variable condenser, shunted across the wires near the loop end, served the purpose of so distributing the current maxima that one position of resonance was secured when the bridge was near the free end of wires.

A study of this method of reception indicated that certain maxima were displaced as the capacity of the bridging condenser was changed; but it was also found that certain other maxima were not shifted in position by this manipulation. The distribution of the current along the wires was very irregular, and one could never be quite positive that the

[2] J. S. Townsend, Phil. Mag. **42**, (1921).

correct successive current maxima had been chosen for the measurement of the half wave. Hours were required to obtain consistent results.

A more rapid and accurate determination of wave-lengths was demanded by the research in progress. A study of the current maxima found by means of a sliding bridge on the simple parallel wire arrangement containing no condenser has revealed a very understandable, rapid and accurate method, and an analysis furnishing a means of rigidly checking results.

In the preliminary tests the permanently mounted pair of wires, closed at one end, were used. The generating circuit was placed at such distances that an amount of energy was transferred to the receiving wires sufficient to give convenient galvanometer deflections. The bridge was moved slowly from one end of the wires to the other, points of maximum deflection being carefully determined by repeated trials.

All current maxima shifted in position for each change in frequency of the exciting oscillations, alternate maxima shifting in opposite directions. All resonance points seemed thus to fall into two groups. If the consecutive bridge positions are numbered from the closed end L_0, Fig. 2, then the *odd* numbered positions L_1, L_3, etc. constitute one group, or set, and the *even* numbered positions L_2, L_4, etc. the other. It was found that $L_3-L_1=L_4-L_2=L_5-L_3$, etc. In one case, for instance, $L_1=93.7$, $L_2=133.7$, $L_3=251.5$, $L_4=291.7$, $L_5=409.4$; hence $L_3-L_1=157.8$, $L_4-L_2=158.0$, $L_5-L_3=157.9$, $L_6-L_4=157.7$. These differences represent the half wave-length of the forced oscillations, the mean error being about .2 per cent.

With the bridge at a point of resonance, a section of the parallel wires including the bridge is vibrating in one of its free modes of oscillation. If the first maximum L_1 shifts to the *left* as the wave-length is increased, then L_2, the second point, will move to the *right*. Evidently each resonance position in the "odd" set indicates the existence of standing waves in that section of the receiver included between the bridge and the "open" ends of the wires. When the bridge is at L_5 the open ends are vibrating in the first free mode; when at L_3, in the second free mode, etc. The same analysis applies to the even numbered positions, with reference here to the bridge and *left*, or closed, end of the receiving wires. When the bridge is at L_2 the closed rectangular circuit at the left is vibrating in its first free mode; when at L_4 the closed loop of length L_4 is vibrating in its second free mode.

The circuit constants which fix the location of these positions of resonance were easily found. The length of wire in the thermo-junction circuit mounted upon the bridge was measured approximately. When

this was added to twice the length of the "open" or free ends of the wires measured from the bridge position corresponding to the fundamental vibration in this part of the circuit, the value was always somewhat less than the half wave-length. Evidently the two open ends, joined by means of the bridge, vibrate as a linear oscillator equal in length to $2(L-L_n)+b$, where L is the total length of the parallel wires, L_n the distance measured from the left end of the wires to the *last* "odd" position of the bridge, and b is the length of the bridge wire. In the closed section at the left, for the first free mode of oscillation, it was found in each case that the total length of the circuit was slightly less than the wave-length. The mean value of λ/p, where $p=2(L-L_n)+b$, was found to be 2.095 for a large number of trials employing various wave-lengths. Likewise, the mean value of λ/P, where $P=2L_2+b+e$, and where e represents the wire spacing, is 1.05. These results are shown in Table I.

Results of More Rigorous Experimental Tests

Certain mechanical defects of the system described and used in the tests given above were thought to be the cause of the non-symmetrical variation in the final ratios exhibited in Table I. Among other hindrances

TABLE I

Wave-length and circuit-length ratios in the open and closed ends of parallel wires, for fundamental mode of vibration.

$\lambda/2$	$L-L_n$	L_2	λ/p	$2\lambda/P$
98.0 cm	36.8	83.5	2.16	2.04
123.9	50.4	103.8	2.05	2.14
155.2	65.3	133.2	2.10	2.12
157.9	64.0	133.3	2.17	2.16
158.5	65.9	136.3	2.12	2.14
161.4	68.8	136.4	2.08	2.16
164.6	68.1	140.6	2.15	2.14
167.1	70.5	14 .6	2.12	2.06
167.6	70.0	144.0	2.13	2.12
171.4	74.2	150.0	2.07	2.10
171.8	73.2	148.2	2.09	2.12
176.7	75.0	153.6	2.11	2.12
180.2	79.3	159.2	2.05	2.08
183.5	80.5	159.6	2.06	2.12
222.0	98.8	201.8	2.07	2.06
224.5	98.0	213.0	2.11	2.10
228.4	100.5	221.6	2.10	2.06
258.7	112.8	230.4	2.05	2.04
265.5	121.8	248.3	2.04	2.02
		Mean values	2.095	2.10

L_n = distance to extreme "odd" position of bridge;
L = total length of parallel wires = 473.0 cm;
p = $2(L-L_n)+b$, where b = length of bridge wire;
P = $2L_2+b+e$, where e = spacing between wires.

was the impossibility of obtaining the equivalent linear dimension of the thermo-junction used. Two additional junctions were made of

constantan and manganin wires .05 mm in diameter and 6 mm in length, crossed at their centers and soldered. One such pair mounted in a hard rubber case 2 cm square and 1.2 cm thick, had the advantages of short length and small mass.

An arrangement of receiving wires was built to permit of easy change in dimensions and terminal conditions. This second Lecher system consisted of two parallel wires, each 386.6 cm long, stretched at a distance of 80 cm above the table. Especially designed wire clamps of small mass were supported by hard rubber strain insulators, and these served as "corner" connectors permitting the opening or closing of the ends of the rectangular circuit at will. The strain insulators could be readily adjusted to give any spacing from 2.5 to 50 cm. The dimensions of this system were in each test obtained to within an estimated error of 1 cm for the total perimeter of the circuit.

The complete vindication of this method as a dependable, accurate and rapid means of measuring wave-lengths, demands that the following requirements be adequately fulfilled. (1) The oscillations emitted by the triode generator must be constant and not affected by the presence of neighboring circuits. (2) No complications in resonance conditions may arise on receiving wires for normal coupling with generator. (3) Neither set of current maxima should be displaced when the end conditions determining the other set are altered. (4) Adequate provision must be made for the resolution of current maxima which sometimes occur near together. (5) Variations in the spacing between the parallel wires, and changes in the size or material must not affect the measured wave-length.

A series of tests were made to determine what effect the coupling between the exciter and parallel wires had upon the intensity and position of the two sets of maxima. With the generator at distances of from 50 to 150 cm and approximately parallel to the receiver, both sets of waves were always obtained regardless of the location of the valve circuit along the table, above, below or on either side of the wires. Moreover the wave-length remained constant within the usual error of measurement. The last conclusion is in accordance with the results obtained by Adolf Sheibe,[3] which appeared subsequent to the completion of the present work. In this connection he says, "We can say, therefore, that the undamped electron vibrations are of great constancy, are reproducible, and scarcely to be influenced by outside circuits."

In the further investigation of those characteristics of the receiving wires which determine the positions of the bridge at resonance, two

[3] Adolf Sheibe, Ann. der Phy. 73, No. 54 (1924)

wave-lengths were employed. The diagram of Fig. 3A indicates a typical example of resonance points using a wave-length of 342 cm with wires spaced at 5 cm. A second test of the same circuit using a wave-length of 212 cm confirmed the analysis indicated, no change occurring in one set when the conditions fixing the other set were changed. In arrangement (a) both ends of the parallel wires are open. At a distance of 79.0 cm from the left end the bridge indicates a maximum of current due to a standing wave set up in the left open end. At 249.6 cm another occurs, due to resonance in the section to the left of this position now vibrating in its *second* free mode. These two positions of resonance are also found in arrangement (c) where the left end is open and the right end is closed. Resonance points 308.2 and 136.9 are each due to the open right end
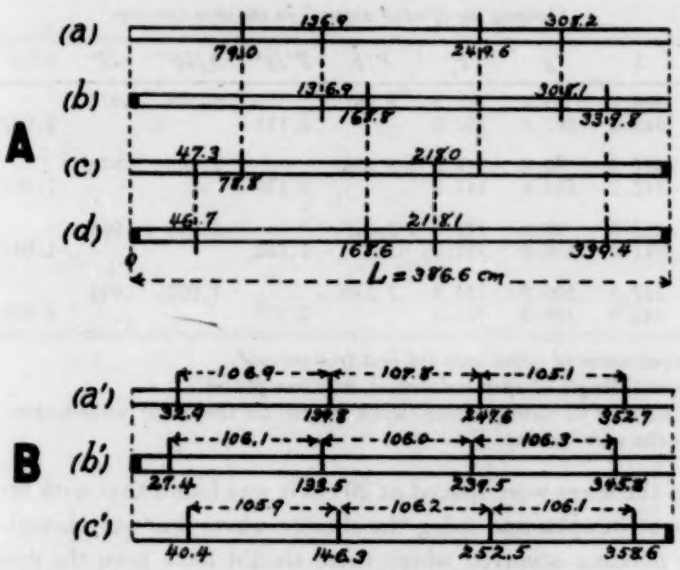
Fig. 3A. Diagram of typical resonance points.
(a) Both ends open; (b) left end closed;
(c) right end closed; (d) both ends closed.

Fig. 3B. Diagram showing overlapping maxima.
(a′) Both ends open, maxima formed by combination of two peaks;
(b′) left end closed; (c′) right end closed.

oscillating in its first and second free modes, respectively. These positions are found in (b), where the *right* end is still open, *left* end closed. Points 168.8 and 339.8 indicate conditions of resonance in the closed left section of the wires. These positions, and those due to resonance in the closed right end, (47.3 and 218.0, c), both persist in (d) where *both* ends are

closed, and in which no resonance points indicated in (a) are to be found, all terminal conditions being different.

Table II indicates the effect of changing the distance between the wires. The first readings at a spacing of 2.5 cm were taken several weeks after the others, when the generator had been used at various other frequencies. The remainder of the series, beginning with the 5 cm spacing, shows the results of operation with no change in the value of the valve circuit constants. All wave-lengths were measured simultaneously on the permanent receiving system used in the earlier work, and in no case were the average values more than 2 mm at variance with those obtained with the second arrangement.

TABLE II

Showing the effect of changes in the wire spacing.

S	λ	p	P	P/p	P'/p'	$\lambda/2p$	λ/P	$\lambda/2p'$	λ/P'
2.5	206.2	93.4	211.3	2.261		1.103	.977		
	345.6	162.6	350.0		2.152			1.062	.988
5.0	212.2	96.8	217.8	2.250		1.096	.976		
	342.2	162.4	347.2		2.139			1.053	.986
10.0	212.0	97.6	221.0	2.265		1.086	.961		
	341.6	164.0	351.2		2.140			1.042	.973
20.0	212.2	100.8	224.8	2.230		1.057	.944		
	342.8	166.5	355.6		2.137			1.029	.965

P = perimeter of *closed* loop for first free period.
p = total length of *open* end circuit, first free period.
P', p', refer to corresponding circuit lengths for the longer wave-length.
S is the wire spacing.

When the wires were spaced at 20 cm it was found that with both ends of the system open and using the shorter wave, *four* very broad-peaked current maxima occurred where there should have been the usual *eight* sharp resonance points. Moreover the half wave-length as indicated by the distance between those maxima showed more variation than usual. By closing first one end of the parallel wires and then the other, it was found that the broad peaks obtained at first occurred at points approximately midway between the sharp maxima due to wave reflection from each of the open ends. The diagram of Fig. 3B indicates the resolution of current maxima in this case. Those maxima due to reflection from the *closed* ends, as in (a) and (c) of Fig. 3A, have been omitted here.

Copper wires of several diameters were tested with the same wave-lengths, and also aluminum wires of corresponding size. In no case was a change in the measured wave-length observed. Using iron wire,

however, satisfactory results were not obtained. The conclusion reached is that the wave-length as measured on the parallel wires is that of the oscillations emitted by the generator, and that no change in wave-length is produced by a change of the diameter of the receiving wires, of the distance between them, or of the material, providing it is non-magnetic and of low resistance.

The writer wishes to acknowledge special indebtedness to Dr. T. T. Smith of the University of Nebraska for his kind suggestions and assistance in the preparation of this paper for publication.

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ADDITIONS TO THE THEORY OF THE HELMHOLTZ RESONATOR

By Arthur Taber Jones

Abstract

The theory of the Helmholtz resonator without a neck assumes that the velocity of the air is everywhere so small that its square may be neglected, and then assumes that at the edge of the mouth the velocity is infinite. In the first addition that is here made to the theory, Helmholtz's proof that the pressure well inside of the resonator does not vary appreciably from point to point is modified (1) by excluding a small ring at the edge of the mouth, and (2) by using equations in which the squares of small quantities are retained. The mathematical procedure is not rigorous, but facts are given that make it seem reasonable. The result is practically the same as that obtained by Helmholtz. In the theory of the Helmholtz resonator it has been customary to make use of Green's theorem. In the second addition to the theory the use of Green's theorem is justified for the case of a resonator without a neck, in spite of the infinite velocity at the edge of the mouth.

Criticisms of the Theory

Introduction. The theory of the Helmholtz resonator involves a curious contradiction, which, so far as I know, has never been pointed out.[1] If it had not happened that the frequency to which the theory leads checks pretty well with that which is found experimentally, attention would no doubt have been called to this inconsistency long ago. In the present paper the contradiction is pointed out, and the theory of the case treated by Helmholtz is so modified as to avoid the contradiction.

The theory of air cavities as resonators was developed by Helmholtz[2] in §10 of his paper on the "Theorie der Luftschwingungen in Röhren mit offenen Enden." The resonators which he considered have no necks, and the communication with the external air is by a hole in an infinitely thin wall. Some dozen years later Rayleigh[3] published a treatment which was simpler than that of Helmholtz, and in which he not only reached the same expression that Helmholtz had found for the frequency of a resonator without a neck, but also extended the treatment to include resonators which have necks of finite length. Grinwis[4] soon afterward

[1] Except in a preliminary report on the present work, Phys. Rev. **23**, 558 (1924)

[2] Helmholtz, Jour. f. reine und angewandte Math. **57**, p. 1, 1860. Reprinted in Helmholtz's Abhandlungen, vol. 1, p. 303, and as vol. 80 of Ostwald's Klassiker der exakten Wiss.

[3] Rayleigh, Phil. Trans. **161**, 77 (1871)

[4] Grinwis, Arch. Néerl. des Sciences, **8**, 417 (1873)

modified Rayleigh's theory with a view to making the treatment more rigorous.[5] Several more recent papers have dealt with particular points in the theory.

Two difficulties in the theory. Helmholtz makes the usual assumption that the velocity of the air is at every point in the field so small that its square may be neglected. With the aid of certain other assumptions he then shows that at any given instant, and with the exception of a small region close to the mouth, the velocity potential throughout the interior of a resonator is practically constant. This amounts to saying that, except close to the mouth, the pressure inside of a resonator does not vary appreciably from point to point. Rayleigh and Grinwis follow Helmholtz in regarding the pressure throughout the interior of a resonator as being the same at all points which are not too close to the mouth, and they therefore implicitly assume[6] whatever Helmholtz has assumed in proving that the pressure is practically constant. It follows that they, too, assume that the velocity of the air is everywhere so small that its square may be neglected.

Rayleigh regards the motion of the air near the mouth of the resonator as represented with sufficient accuracy at any instant by the steady flow of a fluid which is incompressible and devoid of viscosity. For the case of a resonator with a circular mouth and no neck he regards the flow close to the mouth as like that through a circular hole in an infinite plane, and the treatments of Helmholtz and Grinwis are equivalent.

Now it is well known[7] that in the steady flow of an incompressible and non-viscous fluid through a circular hole in an infinite plane, the velocity at the edge of the hole is infinite. Thus the theory of the Helmholtz resonator without a neck involves these two assumptions: First, the velocity of the air is at every point so small that its square may be neglected; second, the velocity of the air at the edge of the mouth is infinite. It hardly seems possible that this contradiction can have escaped Helmholtz and Rayleigh and Grinwis, although none of them mentions it. At one point Helmholtz explicitly assumes that the velocity of the air at every point in the mouth is finite; and Rayleigh[8] in a later paper shows that the assumed distribution of velocity over the mouth cannot be exactly correct,

[5] It may fairly be said, I think, that Grinwis succeeded in making the treatment more rigorous, but his further additions to the theory are not satisfactory.

[6] Rayleigh does not say that when he regards the pressure well inside of the resonator as practically constant he is following Helmholtz. He does say, "A formal proof would require the assistance of the general equations to the motion of an elastic fluid, whose use I wish to avoid in this paper." It may be that he had in mind something different from Helmholtz's work.

[7] See, e.g. Lamb, Hydrodynamics, 3d or 4th ed., Art. 108.

[8] Rayleigh, Roy. Soc. Proc. A92, 265 (1915)

but he says nothing about any difficulty involved in assuming the velocity infinite at the edge.

A second difficulty with the theory lies in the use made of Green's theorem. Rayleigh applies Green's theorem to the velocity potential in a region which extends inside and outside of the mouth, but not far from the mouth; Grinwis applies it to the velocity potential in the inner part of this same region; and Helmholtz applies it to the velocity potential in the entire region inside of the resonator. Now the usual proof of Green's theorem requires, and Helmholtz definitely states this, that neither the function nor its gradient be infinite at any point in the field of integration. This means that Green's theorem is not to be applied to the velocity potential in any region in which the velocity becomes infinite. And yet Green's theorem is applied, by all three authors, to a region in which the velocity is later assumed to be infinite along a certain line.

The infinite velocity at the edge of the mouth is incompatible with the assumption that the velocity is everywhere so small that its square may be neglected, and it also casts doubt upon the legitimacy of the use that is made of Green's theorem.

Modifications of the Theory

The pressure inside of the resonator. Fortunately, it turns out that Helmholtz's theory can he modified so as to indicate rather more certainly that the pressure well inside of the resonator is practically constant, even though the velocity at the edge of the mouth may be infinite. Helmholtz considers a region S which includes the entire space inside of the resonator and is bounded by the walls and the plane of the mouth. Let us exclude from that region a small ring around the edge of the mouth. This ring (Fig. 1) is bounded by a stream surface ss', an equipotential surface pp', a part of the wall, and a part of the plane of the mouth. At no point which is inside of the resonator and outside of this ring, is the velocity infinite. Further, instead of dealing with the total area of the mouth let us deal with an area Ω which consists of that part of the mouth between A and A', plus the area pp' of the bounding equipotential surface. Over all of the area Ω the velocity of the air is finite. Helmholtz's proof may then be adapted to apply to the space as thus modified.

Fig. 1. Mouth of resonator, showing excluded ring.

Helmholtz makes use of the usual equation[9] for simple harmonic standing waves,

$$\nabla^2\varphi+k^2\varphi=0\,, \tag{1}$$

where φ stands for the velocity potential, and k for $2\pi/$(wave-length). This equation assumes that the velocity is everywhere so small that its square may be neglected. Instead of making this assumption let us retain the quantities which we usually neglect, and seek the equation which takes the place of (1). Let ρ stand for the density of the air, p for its pressure, q for its velocity, and u, v, w for the x, y, z components of q; and, following Lamb, let the velocity of the air be the *negative* gradient of the velocity potential. Then the equation of continuity is

$$\frac{\partial\rho}{\partial t}+\frac{\partial}{\partial x}(\rho u)+\frac{\partial}{\partial y}(\rho v)+\frac{\partial}{\partial z}(\rho w)=0\,, \tag{2}$$

and, if a velocity potential exists, the dynamic equation may be written

$$\int\frac{dp}{\rho}=\frac{\partial\varphi}{\partial t}-\tfrac{1}{2}q^2\,. \tag{3}$$

Assume that the motion is adiabatic, so that

$$p=b\rho^\gamma\,, \tag{4}$$

and let a stand for the velocity of sound at points where the disturbance is small, so that

$$a^2=\gamma p/\rho\,. \tag{5}$$

From (3) and (4) eliminate p. From the resulting equation obtain four new equations by differentiating with respect to t, x, y, and z. From these equations and (2) eliminate $\partial\rho/\partial t$, $\partial\rho/\partial x$, $\partial\rho/\partial y$, and $\partial\rho/\partial z$. Make use of (4) and (5). Then in place of the usual wave equation we obtain an equation which may be written

$$\frac{\partial^2\varphi}{\partial t^2}=a^2\nabla^2\varphi+\tfrac{1}{2}\left(2\frac{\partial}{\partial t}+u\frac{\partial}{\partial x}+v\frac{\partial}{\partial y}+w\frac{\partial}{\partial z}\right)q^2\,. \tag{6}$$

If we assume that there are simple harmonic standing waves in which

$$\varphi=\Phi(x\,,\,y\,,\,z)\cos pt\,, \tag{7}$$

(6) leads to

$$\nabla^2\Phi+k^2\Phi=A\sin pt-B\cos^2 pt\,, \tag{8}$$

where

$$A=2p\frac{Q^2}{a^2}\,,\qquad B=\frac{1}{2a^2}\left(U\frac{\partial}{\partial x}+V\frac{\partial}{\partial y}+W\frac{\partial}{\partial z}\right)Q^2\,,\qquad k=\frac{p}{a}\,,$$

[9] I find it more convenient not to follow exactly Helmholtz's notation.

and where U, V, W, Q stand for the amplitudes of u, v, w, q, and are different at different points in space. Since U, V, W, Q are not functions of the time, (8) shows that any motion represented by (7) cannot exactly satisfy (6). That is, we reach a general result that *in no mass of air can there exist pure standing waves in which the amplitude is not small, and in which at the same time the motion is adiabatic and strictly simple harmonic.* Although I do not know that I have ever seen this statement before, the result is probably not to be regarded as new. For in the case of running waves it is known[10] that if the amplitude is not very small the form of the waves is continually changing, and therefore that the motion of the particles of the medium cannot be strictly simple harmonic.

Although expressions of the form (7) cannot exactly satisfy (6), it is true that if the right member of (8) is very small they may come very near to doing so. Let us examine the magnitude of the right member of (8). If the velocity of the air is small compared with that of sound—as will almost always be the case—and if the frequency is not too great, we see that A is small. A is usually more important than B. If we deal with plane waves which are simple and which satisfy (7), it is not difficult to show that B/A is small when the amplitude is small compared with (wave-length)/π; if the waves are spherical, B/A is small when the amplitude is small compared with the distance to the center of the waves, provided that the point which we are considering is not too far from that center. These facts seem to indicate that unless the amplitude is very great, we shall be justified in neglecting the last term in (8) and in assuming that the first term on the right is very small.

Moreover, we shall not change the order of magnitude of the right member of (8) if we replace $A \sin pt$ by $A \cos pt$. If we make this change, and neglect the last term in (8), we are led to the equation

$$\nabla^2\varphi + k^2\varphi = 2pq/a^2. \tag{9}$$

If, instead of assuming, as Helmholtz does, that (1) holds, we assume that (9) holds, we shall be in error, but we shall feel tolerably sure that (9) is more nearly correct than (1), and that the second member of (9) is of the right order of magnitude. If then in Helmholtz's work we are able to replace (1) by (9) and show that the result is not changed, we shall in a way have justified Helmholtz's result. This proves to be possible.

We find that we must modify the first equation in Helmholtz's §10,[2] and that the terms which we introduce into his equations (28) and (28a) are negligibly small. Consider first his (28). Omitting two terms which

[10] See e.g. Rayleigh, Theory of Sound, Art. 250, and Phil. Mag. 10, 364 (1905)

are negligible whenever k^2r^2 is small compared with unity, the equation which takes the place of (28) is, in our present notation,

$$\int \frac{\partial \varphi}{\partial n} d\omega = -\frac{k^2}{3} \int \varphi r \frac{\partial r}{\partial n} d\omega - \frac{2p}{a^2} \iiint q^2 dx dy dz , \qquad (10)$$

where ω refers to the area of the bounding surface, r is the distance of the point in question from the origin, and the normal n is drawn inward.

If the resonator is spherical, of radius r_1, with the origin at its center, and if we denote average values over the boundary by a subscript b, and average values throughout the volume by a subscript v, (10) becomes

$$q_m \Omega = \tfrac{1}{3} k^2 \varphi_b r_1 \cdot 4\pi r_1^2 - (2p/a^2) q_v^2 \cdot \tfrac{4}{3}\pi r_1^3, \qquad (11)$$

where q_m stands for the average velocity of the air outward across the surface Ω at the mouth. For plane waves it is easy to show that φ is of the order q/k; and for spherical waves, not far from the center of the waves, that it is of the order qr_c, where r_c stands for the distance to the center of the waves. From these facts, and assuming that q_v and q_b are of the same order of magnitude, it is easy to show that if the waves were plane the third term in (11) would be small compared with the second whenever the velocity of the air is small compared with the velocity of sound; and that if the waves were spherical, the third term would be small compared with the second whenever the amplitude is small compared with the distance to the center of the waves. That is, if the waves were either plane or spherical, the last term in (11) would be negligible unless the intensity of the sound was enormous. In the actual case of a resonator we are then probably justified in neglecting the last term in (11), and therefore in neglecting also the last term in (10). That is, the equation which we obtain is the same as that which Helmholtz uses.

Next consider Helmholtz's (28a). Here we find that we must introduce a term which will be negligible under practically the same conditions under which the third term in (11) may be neglected. Thus we reach Helmholtz's (28a).

We have given up the assumption that the velocity of the air is everywhere so small that its square may be neglected, and have replaced it by the assumption that, except close to the edge of the mouth, the velocity of the air is small compared with the velocity of sound. With this new assumption we have been able to modify Helmholtz's theory so as to give us more confidence that well inside of a resonator the pressure does not vary appreciably from point to point.

The use of Green's theorem. Our next problem is to justify the application of Green's theorem to a region which includes the edge of the mouth,

where the velocity is infinite. Let us divide the region in the neighborhood of the mouth into two parts. Let one of these parts be a ring similar to that in Fig. 1, but extending, if it is Rayleigh's use of the theorem that we are justifying, symmetrically on both sides of the plane of the mouth. Then in the region close to the mouth and outside of this ring, the velocity of the air is finite and Green's theorem may be applied.

What about the region inside of the ring? We are concerned with the integral

$$\iiint \left\{ \left(\frac{\partial \varphi}{\partial x}\right)^2 + \left(\frac{\partial \varphi}{\partial y}\right)^2 + \left(\frac{\partial \varphi}{\partial z}\right)^2 \right\} dx dy dz \,. \tag{12}$$

In spite of the infinite velocity at the edge of the mouth, it may be possible to show that the value of this integral decreases indefinitely with the volume of the ring. If that is the case, the value of the integral over the ring may be made as small as we please; and since in the rest of the region the velocity is finite, Rayleigh's procedure will be justified.

In order to integrate throughout the volume inside of the ring it is convenient to change to ellipsoidal coordinates. Let us take the x axis as perpendicular to the plane of the mouth, and passing through the middle point of the mouth; and, following the notation used by Lamb,[11] let us set

$$x = k\mu\zeta, \quad \varpi^2 = y^2 + z^2 = k^2(1-\mu^2)(\zeta^2+1). \tag{13}$$

Then the surfaces $\zeta = \text{const.}$ are oblate ellipsoids of revolution, the surfaces $\mu = \text{const.}$ are hyperboloids of revolution of one sheet, and all of these surfaces have the common focal circle $x=0$, $\varpi = k$. The general distribution of the surfaces is shown in Fig. 2.

If δs_ζ stands for the perpendicular distance between the surfaces $\zeta = \text{const.}$ and $\zeta + \delta\zeta = \text{const.}$, and δs_μ for the perpendicular distance between $\mu = \text{const.}$ and $\mu + \delta\mu = \text{const.}$, Lamb shows that

$$\delta s_\zeta = k\sqrt{\frac{\zeta^2+\mu^2}{\zeta^2+1}}\delta\zeta \,, \qquad \delta s_\mu = k\sqrt{\frac{\zeta^2+\mu^2}{1-\mu^2}}\delta\mu \,. \tag{14}$$

For the steady flow of an incompressible and non-viscous fluid through a circular hole in an infinite plane, Lamb shows[7] that the velocity potential is given by

$$\varphi = A \cot^{-1}\zeta, \tag{15}$$

where A is some constant. Thus the surfaces $\zeta = \text{const.}$ are equipotential surfaces.

[11] Lamb, Hydrodynamics, 3d or 4th ed., Art. 107.

The integrand in (12) is then $(\partial\varphi/\partial s_\zeta)^2$, and by using (14) and (15) we see that this becomes

$$\left(\frac{\partial\varphi}{\partial s_\zeta}\right)^2 = \frac{\zeta^2+1}{k^2(\zeta^2+\mu^2)}\left(\frac{\partial\varphi}{\partial\zeta}\right)^2 = \frac{A^2}{k^2(\zeta^2+\mu^2)\,(\zeta^2+1)}\,.$$

The element of volume may be written $2\pi\varpi\delta s_\zeta\delta s_\mu = 2\pi k^2(\zeta^2+\mu^2)\delta\zeta\delta\mu$, so that (12) becomes

$$2\pi kA^2\iint\frac{d\zeta d\mu}{\zeta^2+1}\,. \tag{16}$$

In the ring the limits of integration for ζ are a negative value of ζ and

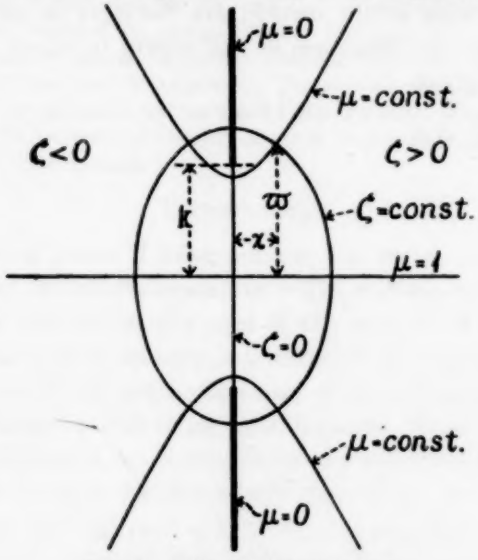

Fig. 2. Ellipsoidal coordinates.

an equal positive value, say ζ', and for μ they are zero and a positive value, say μ', so that (16) becomes

$$4\pi kA^2\mu' \tan^{-1}\zeta'. \tag{17}$$

Since decreasing μ' and ζ' makes the ring smaller, (17) shows that by choosing μ' and ζ' sufficiently small we may cause the contribution which the ring makes to the integral (12) to be smaller than any assigned quantity. Thus the application of Green's theorem to the velocity potential throughout the region near the mouth of the resonator is justified, even though we later assume a certain distribution of velocity which makes the velocity at the edge of the mouth infinite.

Since the infinite velocity at the edge of the mouth does not invalidate Rayleigh's theory for the case of a resonator without a neck, it seems likely that if we deal with resonators which have necks the infinite

velocity which is involved at sharp corners will also leave the theory valid. I have not attempted to justify the use of Green's theorem in such cases.

It seems hardly necessary to point out that, in spite of the rather good agreement between the pitches found for resonators experimentally and the pitches calculated from the theory, an infinite velocity at the edge of the mouth cannot actually occur. In fact, Osborne Reynolds[12] has shown that the maximum velocity which can be attained in the flow of a compressible fluid equals the local velocity of sound. That the theory of the Helmholtz resonator, containing the assumption of an infinite velocity at the edge of the mouth, fits the facts as well as it does, is probably due to the smallness of the region in which the theoretical velocity is very great.

SMITH COLLEGE,
December 23, 1924

[12] Osborne Reynolds, Phil. Mag. 21, 185 (1886)

THE FREQUENCY OF A HELMHOLTZ RESONATOR WITH A HYPERBOLOIDAL MOUTH

By Arthur Taber Jones

Abstract

It is shown theoretically that if the circular hole in a resonator is replaced by a hyperboloidal mouth which reduces the flux in the ratio $(1-\mu_1)$, the frequency is reduced in the ratio $[(1-\mu_1)/(1+\mu_1)]^{1/4}$. The ratio of the greatest velocity—which occurs close to the wall at the narrowest section—to the velocity at the middle of the section is $1/\mu_1$. The lowering of pitch is given for six hyperboloidal mouths. Eight experimental determinations of frequency were made with two brass hyperboloids. The greatest difference between the observed and the calculated pitches was 0.3 of a half step. This agreement indicates that the viscosity of the air, which is neglected in the theory, has little effect on the frequency.

Introduction

In the preceding paper[1] I have pointed out certain difficulties in the theory of the Helmholtz resonator. These difficulties arose in part from an infinite velocity at the edge of the mouth. When a resonator has no neck this infinite velocity is introduced by regarding the motion of the air close to the mouth as like that of an incompressible and non-viscous fluid through a hole in an infinite plane. Now an infinite plane with a circular hole in it is a limiting case of a hyperboloid of revolution, and the stream surfaces for the steady flow of an incompressible and non-viscous fluid through such a hole are confocal hyperboloids. These facts suggested the possibility that in the theory of the resonator we might be able to replace the circular hole in an infinite plane by a very flat hyperboloid, and so avoid the infinite velocity and yet not change greatly the calculated pitch to which the resonator responds most vigorously.

This hope has not been fulfilled, but a theoretical expression for the frequency of a resonator with a hyperboloidal mouth has been developed, and a few experimental tests of the expression have been made.

Theory

Rayleigh's expression[2] for the frequency N to which a Helmholtz resonator responds most strongly is

$$N=(a/2\pi)\sqrt{c/S}\,, \tag{18}$$

[1] For simplicity of reference, the equations and figures are numbered consecutively throughout the two papers.

[2] Rayleigh, Phil. Trans. **161**, 77 (1871) or Theory of Sound, Art. 304.

where a stands for the velocity of sound, c for the conductivity of the mouth, and S for the volume of the resonator. When the mouth is regarded as a circular hole in an infinite plane, we have

$$c = 2R, \tag{19}$$

where R stands for the radius of the hole.

As in the preceding paper let us use the ellipsoidal coordinates defined by (13) and represented in Fig. 2. If any one of the stream surfaces $\mu = \text{const.}$ is made rigid, there will be no change in the motion of the air inside of that surface. It follows that we may compare the flux through this hyperboloid with that through the entire hole, and then compare the conductivity of the hole with that of another hole which has the same diameter as the narrowest part of the chosen hyperboloid, and so determine the conductivity of the given hyperboloid when it is used as a mouth for a resonator.

To carry out this plan we need first an expression for the distribution of the velocity u throughout the hole. It is known[3] that this distribution is given by

$$u = A/\sqrt{k^2 - \varpi^2}\,, \tag{20}$$

where A is a constant. The flux F through the part of the hole which is inside of a circle of radius r is

$$F = \int_0^r u \cdot 2\pi\varpi d\varpi\,,$$

or, using (20),

$$F = 2\pi A\left[k - \sqrt{k^2 - r^2}\right]. \tag{21}$$

We are now to use (21) twice, once with r standing for the radius of the narrowest part of a hyperboloid, and once with r standing for the radius of the focal circle. To find the family of hyperboloids, we eliminate ζ from the equations (13), and so obtain

$$\frac{\varpi^2}{1-\mu^2} - \frac{x^2}{\mu^2} = k^2\,. \tag{22}$$

Let us choose for the mouth of the resonator the hyperboloid $\mu = \mu_1$, and let the radius of the narrowest part of this hyperboloid be R. Then for $x = 0$ we have $\varpi = R$, and (22) gives

$$R^2 = k^2(1 - \mu_1^2). \tag{23}$$

The radius of the focal circle is k. From (21) it follows that the ratio of the flux through the chosen hyperboloid to the flux through the entire hole is simply

$$1 - \mu_1. \tag{24}$$

[3] Lamb, Hydrodynamics, 3d or 4th ed., Art. 108.

To find the ratio between the conductivity of the hyperboloid and that of a simple hole of equal radius, we multiply (24) by the ratio of the conductivities of two holes, one having a radius k and the other a radius R. Eq. (19) shows that the ratio of the conductivities of these two holes is k/R, so that the ratio between the conductivity of the hyperboloid and that of a hole of equal diameter is

$$(k/R)(1-\mu_1),$$

or, if we use (23) to eliminate k,

$$\sqrt{\frac{1-\mu_1}{1+\mu_1}}.$$

From (18) and (19) it follows that the frequency of a resonator when equipped with a hyperboloidal mouth is

$$N=(fa/2\pi)\sqrt{2R/S},$$

where f is defined by

$$f=\sqrt[4]{\frac{1-\mu_1}{1+\mu_1}} \tag{25}$$

This quantity f represents what we may call the *lowering of pitch* produced by using for the mouth of the resonator a hyperboloid instead of a simple hole. Thus if $f=2/3$, the resonator responds to a note which is a musical fifth below that to which it would respond if the wall near the mouth were a plane of zero thickness, and the mouth were simply a circular hole with a radius equal to that of the narrowest part of the hyperboloid.

The greatest velocity inside of the hyperboloid occurs close to the wall at the narrowest section. To find this greatest velocity let us call the velocity at the middle of the narrowest section u_0. This determines the constant A in (20) as equal to u_0k; and for $\varpi=R$ (20) and (23) give as the maximum velocity

$$u_{max}=u_0/\mu_1 . \tag{26}$$

Fig. 3 shows the shape of mouth for a number of cases. Table I shows the lowering of pitch by each of these mouths, and gives the corresponding value of u_{max}/u_0. It will be seen that with a very flat hyperboloid the lowering of pitch depends to such an extent on the precise hyperboloid which is chosen, that when the mouth is simply a circular hole in a wall of finite thickness it is not feasible to choose *a priori* any particular hyperboloid as representing the actual mouth.

Experimental

In order to test the above theory two brass hyperboloids were prepared. Two resonators were used, each of which was a glass bottle with the bottom cut off, and with a brass ear piece fastened to the neck. The diameter of each hyperboloid varied from a little less than 15 mm at the narrowest section up to about 6 cm, and the overall heights

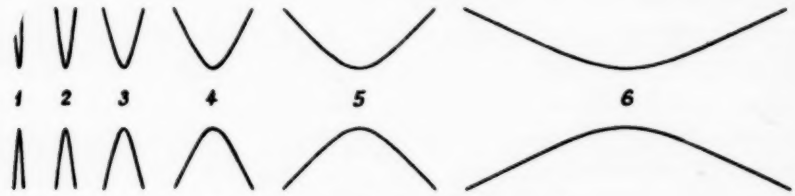

Fig. 3. Various hyperboloidal mouths.

were about 3 cm and 6 cm. It was intended that one hyperboloid (A) should lower the pitch a perfect fifth, and the other (B) a major third. When the hyperboloids were measured, before fastening them onto the bottles, it was found that the shape of A was fairly satisfactory, but that B was not so nearly a hyperboloid. The most important part of the mouth, in determining the pitch, is the part nearest

Table I

Lowering of pitch, maximum velocity.

Mouth	u_{max}/u_0	Lowering of pitch
1	17.32	Quarter step (equally tempered)
2	8.70	Half " " "
3	4.41	Whole " " "
4	2.39	Major third (not tempered)
5	1.49	Fifth " "
6	1.13	Octave

to the narrowest section. For the shape of A readings were used which extended to $\varpi = \pm 18$ mm, but the most weight was given to readings which extended only to $\varpi = \pm 9$ mm. For B the readings which were used extended to $\varpi = \pm 14$ mm. The values that were adopted as representing best the theoretical lowering of pitch by these particular mouths were 0.664 for A, and 0.76 for B. Both of these values are probably to be trusted to the second figure after the decimal point.

There is always some question as to what should be taken for the volume of a resonator. In the cases of resonators which have necks Rayleigh included half the volume of the neck. With the hyperboloidal mouths I have taken the volume to the narrowest part of the hyperboloid.

The volumes were determined by weighing the water which the resonators would hold.

To determine the pitch of maximum response I tried several methods, and finally followed Rayleigh, using a reed organ and playing notes an octave below those to which the resonator responded. I found, as Rayleigh did, that it is easier to feel sure of the relative intensities when the resonator is responding to the octave than when it is responding to the fundamental; and I also found, as he did, that there is little difficulty in locating the pitch of maximum response within a quarter of a half step.

Two determinations of the pitch of maximum response were made for each resonator, and then the mouths were interchanged and two more determinations made for each. The results are shown in Table II. It will be seen that the observed frequencies agree remarkably well with the calculated.

TABLE II

Comparison of calculated and observed frequencies

Mouth	Bottle	Volume	Temperature	N_{calc}	N_{obs}	Difference (mean half steps)
A	1	587.4 cc	17.5°C	180.4	183	+0.2
A	1		19.1	180.9	183	+0.2
B	2	208.1	17.5	349.5	351	+0.1
B	2		19.5	351.0	349	−0.1
A	2	221.7	20.5	295.4	297	+0.1
A	2		20.0	295.2	300	+0.3
B	1	572.6	20.5	211.8	216	+0.3
B	1		20.1	211.6	215	+0.3

I had some fear that with mouths of this sort the viscosity of the air might be important. In the steady flow of an incompressible and non-viscous fluid through a circular hole in an infinite plane the velocity is distributed in accordance with (20), and so is a minimum at the middle of the hole. If the fluid is viscous R. A. Sampson[4] has shown that the distribution of velocity is entirely different, vanishing at the edge and being a maximum at the middle of the hole, and that this distribution is independent of the magnitude of the viscosity. Since the air is not absolutely devoid of viscosity, it would seem that (20) could not represent the actual distribution of velocity. Moreover, by filling a resonator with smoke and observing it stroboscopically, Dvořák[5] found vortices formed outside of the resonator when the air rushes outward, and inside of it when the air rushes inward. These facts seemed to indicate that the viscosity of the air

[4] R. A. Sampson, Phil. Trans. A182, 449 (1891)
[5] Dvořák, Phys. Zeits. 2, 490 (1901)

is of some importance, but I have found no satisfactory theoretical way of taking the viscosity into account, and in spite of this neglect the theoretical frequencies turn out to agree very satisfactorily with those which are observed experimentally. It seems probable that the smallness of the viscosity of the air prevents the establishing of anything approaching the distribution of velocity which would obtain in the steady flow, and so makes the actual distribution of velocity much more nearly like that of a fluid which has no viscosity.

SMITH COLLEGE,
December 23, 1924

BOOK REVIEWS

The Earth, its Origin, History and Physical Constitution. By HAROLD JEFFREYS, St. John's College, Cambridge, England.—This book is an important contribution to the science of geophysics. The author has succeeded admirably in his avowed purpose to present an outline of the major problems concerning the physical constitution of the Earth and the phenomena of isostasy and mountain-building, and to mold the various phases of geophysics into a harmonious system.

Like the life of Tristram Shandy this story of the Earth begins with its prenatal history. There now seems little doubt that the planets were formed through tidal disruption of the parent sun by the close approach of another star. The particular theory adopted by the author differs from the form as originally developed by Chamberlin and Moulton and resembles more that advanced by Jeans. The scope of the book is shown by the list of chapter-headings: The Nebular Hypothesis of Laplace; The Tidal Theory of the Origin of the Solar System; The Origin of the Moon; The Resisting Medium; The Age of the Earth; The Thermal History of the Earth; The Equations of Motion of an Elastic Solid with Initial Stress; The Bending of the Earth's Crust by the Weight of Mountains; The theory of Isostasy; The Thermal Contraction Theory of Mountain Formation; Theories of other Surface Features; Seismology; The Figures of the Earth and Moon; Tidal Friction; The Variation of Latitude, and also (in the Appendix), The Planetesimal Hypothesis; Jeans's Theory; The Hypothesis of the Indefinite Deformability of the Earth by Small Stresses; Theories of Climatic Variation; Empirical Periodicities.

The chapter on the thermal history of the Earth is an excellent example of the stimulating treatment of a difficult subject. The author has been far-sighted enough to see the value of Holmes' method of reconciling the present-day temperatures in the Earth with the known and important heat-evolution due to the radioactive materials in the crust.

The value of the book is enhanced by the author's readiness to express his own opinion on the various disputed questions. The book is not a compilation of undigested facts. The author admits that it probably will fail "to instruct the specialist in the data of his own subject," and these same specialists no doubt will take issue with the author on several minor points such as his treatment of the physical properties of glasses on p. 115; nevertheless his hope that the specialist will be enabled "to check a hypothesis by means not only of his own data, but by some of those of related subjects" seems assured of fulfillment.

A pleasing touch is given by the quotations with which each chapter is headed. A particularly happy one from Lewis Carroll introduces the Theory of Isostasy:

> "*I* could show you hills, in comparison with which you'd call that a valley."
>
> "No, I shouldn't," said Alice, surprised into contradicting her at last: "a hill *can't* be a valley, you know. That would be nonsense. . . . "
>
> The Red Queen shook her head. "You may call it nonsense if you like," she said, "but *I've* heard nonsense, in comparison with which that would be as sensible as a dictionary!"—Pp. ix+278. Macmillan Co. 1924. L. H. ADAMS

Über Wärmeleitung und Andere Ausgleichende Vorgänge. By Emil Warburg.—In writing this little book the author has in mind the needs of the experimental physicist and the technician. He presupposes on the part of the reader a knowledge of experimental physics and of the fundamentals of calculus.

A short introduction deals with the concept and properties of equalizing phenomena whose common characteristic is their irreversibility, phenomena such as the equalization of differences in temperature through heat conduction and radiation, in velocity through friction, in concentration through diffusion, and in potential within homogeneous substances through electrical conduction. Part I gives the foundation of the general theory of heat conduction with a derivation of the fundamental differential equation based upon Fourier's hypothesis; boundary conditions and formulas involving external conductivity are also given. Part II considers stationary flow under various conditions, including point sources, and gives a proof of the uniqueness of temperature determination. A number of methods for obtaining the thermal conductivity of a substance are explained, as well as the theory of the bolometer and practical points concerning thermal insulation. Problems relating to the variable state in semi-infinite and infinite media are given in Part III. These include earth cooling, with and without modification due to radioactivity, and Fourier Series. Part IV is taken up with the general theory and application of viscosity.

Throughout the different chapters numerous examples illustrating applications of the different formulas are made. The author gives references to many original papers on the various phases of the subject. A reference might also have been made to Fourier's classical work Théorie Analytique de la Chaleur or to the German translation published in 1884, by Julius Springer.—Pp. x+106. $1.40. Julius Springer, Berlin, 1924.

O. J. Zobel

Handbook of Mathematical Statistics. By H. L. Rietz, H. C. Carver, A. R. Crathorne, W. L. Crum, J. W. Glover, E. V. Huntington, T. L. Kelley, W. M. Persons, A. A. Young, members of a National Research Council committee on statistics.—This is an admirable example of a type of handbook that is too rare. A mathematical introduction is followed by chapters on frequency distribution, interpolation, curve fitting, random sampling, correlation, periodogram analysis, index numbers, etc. The material is comprehensive and is presented in very compact form, mostly without proofs but with abundant references. The beginner will find the book useful, not as a text, but as a guide, while to one with some experience it should be invaluable.—Pp. 221. $4.00. Houghton, Mifflin Co.

E. H. Kennard

Dynamo Electric Machinery. By Erich Hausmann.—This is a complete text covering both direct and alternating current machinery for engineering students. It supplants two volumes written jointly with the late Samuel Sheldon entitled Direct Current Machines and Alternating Current Machines, being virtually a new edition of these well known and popular books. The book contains the usual chapters dealing with electric and magnetic circuits and the properties of alternating currents. It is first class as a general text. In its evolution it has benefited by the process of elimination and survival; the style is straight-forward and clear. Whether the use of such terms as abcoulombs, and abstatamperes, adds or detracts from the book is a matter of individual opinion.—Pp. 645, 445 figs. Price $4.50. D. Van Nostrand Co., 1924.

Frederick Bedell

Electrical Measuring Instruments and Supply Meters. By D. J. Bolton.—Without going too far on either the purely theoretical or the purely commercial side, the author describes various types of indicating and supply instruments. His aim has been to adequately explain the operation of all types of instruments in general use, with a view to meeting the needs of the general engineer, rather than the research or manufac-

turing specialist, but others besides engineers should find the book useful. The descriptions are clear and adequate and in remarkably short compass the author has given the reader a good idea of the theory and operation of a wide variety of instruments. The instruments illustrated are now being manufactured in Great Britain,—with some exceptions, as in the case of supply meters—so that the book may be looked upon as a summary of current British practice. Adequate references would have added immensely to the value of the book.—Pp. 328, 180 figs. Price $5.00. E. P. Dutton and Co., 1923.

FREDERICK BEDELL

L'Origine Tourbillonnaire de L'Atome et ses Consequences. BY JEAN VARIN D'AINVELLE.—The author of this book reverts to the idea of a fluid ether in which atoms set up vortex tubes by their rotation. The ether is supposed to possess the properties of viscosity and compressibility and to be influenced by changes of temperature. It resides upon a stratum of sub-ether of a more fundamental nature. The author attempts to interpret the simpler aspects of the Bohr theory in terms of vortex tubes. The treatment of the subject is descriptive and qualitative rather than mathematical and quantitative.—Pp. 214, Gauthier-Villars et Cie, Paris, 1924. LEIGH PAGE

PROCEEDINGS

OF THE

AMERICAN PHYSICAL SOCIETY

MINUTES OF THE PASADENA MEETING, MARCH 7, 1925.

The 132nd regular meeting of the American Physical Society was held in Pasadena, at the California Institute of Technology, in the Norman Bridge Laboratory of Physics, on Saturday, March 7. The presiding officer was Professor R. A. Millikan.

The session consisted of 28 papers, of which abstracts of 27 are given in the following pages. An **Author Index** will be found at the end.

The attendance was 120.

DAVID L. WEBSTER
Local Secretary for the Pacific Coast

ABSTRACTS OF PAPERS

1. The Compton effect with hard x-rays. D. L. WEBSTER and P. A. ROSS, Stanford University.—Graphs of ionization spectra are presented, supplementing the authors' statement at the December meeting that the Compton effect exists for tungsten K-series rays and the adjacent continuous spectrum. In glass the Compton shifted component is several times as strong as the unshifted, and in graphite still stronger. In silver, the fluorescent rays were very strong but the scattered too weak to measure. The wave-length shifts confirm Compton's theory within limits of error (about 0.03 angstrom).

2. Characteristic x-rays from lithium. G. K. ROLLEFSON, University of California.—A method which has been described previously (Phys. Rev. **23**, 35, 1924) has been used to determine the critical potentials corresponding to the excitation of characteristic x-rays of lithium. Definite critical potentials have been obtained at 39.2, 43.05 and 46.0 volts, and it is shown by comparison with the known energy levels for three electron systems that these correspond to the differences $1_1 \rightarrow 2_1$, $1_1 \rightarrow 2_2$, and $1_1 \rightarrow 3_1$ respectively. Some evidence has also been obtained for a higher critical potential which probably represents ionization of the 1_1 level. The 2_2 to 1_1 transition corresponds to the Kα line of lithium. Using this value for Li and Lukirsky's value for the Kα line of carbon, it is possible to extend the Moseley curve for the Kα line and obtain the values for the other light elements by interpolation. The following are the ν/R values for the light elements: Li, 3.18; Be, 6.86; B, 12.25; C, 18.60; N, 27.46; O, 37.21; F, 48.44; Ne, 61.31.

3. Unusual x-ray reflections on spectral photographs. LINUS PAULING, California Institute of Technology.—On a photograph of the molybdenum K-radiation reflected from planes (001) of the orthorhombic crystal $UO_2(NO_3)_2 6H_2O$, several weak lines were found which did not give the same value of d/n as the strong reflections. These lines were not due to reflection in the usual way from other planes, for they persisted even after a change in orientation of the crystal and the use of a slotted screen. The explanation of their origin is that previously advanced by Dickinson in explanation of diffuse spots on Laue photographs, that there are present in or on an easily deformed crystal minute crystals whose axes make small angles with those of the large crystal, the number of these being greater the smaller the angles. A strong photograph made with a water-cooled tube showed this predicted sort of powder pattern being focused to produce the unusual lines. Similar lines have been found with other crystals, notably KI. These lines may have introduced errors in the interpretation of spectrographic and spectrometric measurements.

4. The series spectra of two-valence-electron atoms of phosphorus (P_{IV}) sulphur (S_V) and chlorine (Cl_{VI}). I. S. BOWEN and R. A. MILLIKAN, California Institute of Technology.—With the aid of the irregular and the regular doublet laws which we have previously found useful for the prediction of the spectra of stripped atoms (atoms denuded of all valence electrons save the one which in moving back and forth between energy levels gives rise to the observed radiation) we have now been able to make similar identifications for a new series of atoms, of like electronic structure but containing in each case two electrons in the outer shell instead of one. Thus we have definitely identified 23 lines and 12 term-values of P_{IV}, 17 lines and 8 term values of S_V, and 6 lines of Cl_{VI}. It has further been found that the pp' group follows the irregular doublet law, and with the aid of this law this group has been traced from Mg_I to Cl_{VI}. That this group follows the irregular doublet law means that all jumps involved must be between orbits of the same total quantum number, viz., 3 in the case of the Mg to Cl sequence, and 2 in the case of the Be to O sequence. This definitely eliminates any jump involving d levels in the latter sequence and hence renders Wentzel's explanation and selection principle unacceptable.

5. The series spectra of three-valence-electron atoms of phosphorus (P_{III}) sulphur (S_{IV}) and chlorine (Cl_V). R. A. MILLIKAN and I. S. BOWEN, California Institute of Technology.—By the methods mentioned in the preceding abstract, 21 lines and 10 term values of P_{III} have been definitely identified; also 20 lines and 10 term values of S_{IV}; also 10 lines of Cl_V. Further, a quadruplet pp' group, in which the $p_1'p_2'$ separation is about two-thirds of the p_1p_2 separation, has been discovered and traced from P_{III} to Cl_V and from C_{II} to O_{IV}. This new pp' group also follows the irregular doublet law. Again, the triplets arising from atoms of similar electronic structure but varying effective nuclear charge have been everywhere found to follow the fourth power relativity law as closely as do the doublets.

6. The widening phenomena of spectrum lines as related to temperature classification and energy levels. ARTHUR S. KING, Mount Wilson Observatory.—A close parallelism is found between the temperature classification of electric furnace lines and that based on widening effects in sources of high electrical excitation, such as the disruptive spark, pole of the arc, and the thousand-ampere arc. In the latter sources, low-temperature lines remain nearly symmetrical, while those responding to higher temperatures are distinguished by increasing degrees of dissymmetry and diffuseness. It follows that the "multiplet" groups, whose selection and assignment to energy levels are based largely on the temperature classification, show in the discharge sources a definite increase in sensitiveness to wave-length disturbance as higher energy levels are

involved. About fifty multiplets of iron, examined in the high-current arc, illustrate this clearly. The tendency to widening, usually with dissymmetry, does not result necessarily from large difference of energy levels passed through, but depends on the initial stage, as if the larger electronic orbits were especially sensitive to perturbation caused by high excitation. Iron multiplets starting from the three lowest levels are affected but slightly, while those from higher levels show increasing degrees of dissymmetry. Lines of a given multiplet are affected nearly alike, so that the differences in widening effect supplement the temperature classification as a means of grouping the high-level lines.

7. Standard wave-lengths in the spectrum of iron. HAROLD D. BABCOCK, Mount Wilson Observatory.—With the apparatus and methods previously described, the investigation reported last June has been continued. Interferometer measurements on about 150 lines distributed through the visible spectrum have been secured, confirming and extending the preliminary results. Systematic differences are found between the new measurements and the adopted system of secondary and tertiary standards, amounting to about 0.002 A for $\lambda < 5500$ A, but averaging about 0.008 A in the red, the new measures being shorter than the old. Although this accords with the work of other observers in showing that the adopted system is too high, there are definite systematic differences between the measurements made at Mount Wilson and those at the Bureau of Standards, amounting to 0.003 A for the red lines, which are dependent on differences in the iron arcs used. The distinguishing features of the adopted type of iron arc are illustrated.

8. The absorption spectrum of oxygen to 1240 A. J. J. HOPFIELD and S. W. LEIFSON, University of California.—The intense continuous spectrum of hydrogen discovered by Lewis was used as a background in a part of the region λ2000—1250. With 2.5 cm of oxygen at atmospheric pressure, sixteen clearly resolved bands appear between λλ1950 and 1760. This is the first verification of the work of Schumann, who found 14 bands at λ1850. This appears to be the first time that the wave-lengths of these bands have been determined. They may be accurately measured on our spectrograms. The approximate wave-lengths of the heads are λλ1950, 1929, 1908, 1888, 1869, 1851, 1836, 1821, 1808, 1797, 1788, 1780, 1773, 1768, 1764, and 1762. A fine structure of these bands has also been observed. The great absorption band at λ1750—1300 is of course registered on our plates. The vacuum grating spectrograph previously employed by one of us was used in this work. Preliminary investigations on other substances are now in progress.

9. A preliminary report on the application of the combination principle to the bands of the Swan group of carbon. J. D. SHEA, University of Californa.—These bands are found in the spectra of stars of spectral class R and N. Vibration quantum numbers previously assigned by Birge to the various bands of the Swan group have been tested by means of the combination principle. The existing series for the four bands with heads at λ5165, 5129, 5635, and 5585 have been extended and improved. These particular bands correspond to vibration quantum changes in emission of 0 to 0, 1 to 1, 0 to 1, and 1 to 2, respectively. The origin of these bands has been located. Thus for the λ5165 band it is 14 lines or 4.8A from the head. The combination principle has been successfully applied to these four bands. Since it is not possible to resolve the line in the vicinity of the head, it is possible to obtain only an approximate value for the moment of inertia as follows, $J' = 16 \times 10^{-40}$ gm cm², $J'' = 17 \times 10^{-40}$ gm cm². These values give a separation of the two atoms forming the molecule of 1.3×10^{-8} cm, when the molecule is assumed to be C_2. The values given are undoubtedly accurate to the number of figures given.

10. The band spectra of coupled systems. H. KAHLER, National Research Fellow, California Institute of Technology.—The spectra of the crystals containing uranium oxide as a constituent consist of bands in the blue side of the spectrum having an approximately constant frequency interval and associated bands in the longer wave-length region with a different frequency interval. It is shown that such results are to be expected when the cross product terms involving the quantum numbers of the nuclear and electronic vibrations are taken into consideration. The effect of coupling is shown to lead to a formula which represents the data of Henri on the spectra of polyatomic gases. The multiple linear terms of Henri were hardly reconcilable with previous considerations.

11. Behavior of bright hydrogen lines in stellar spectra. PAUL W. MERRILL, Mount Wilson Observatory.—Among the hotter stars the bright hydrogen lines are usually double with a separation of 2 to 4 angstroms. In one star the violet component of $H\beta$ varies periodically in intensity, while the other component remains unchanged. In all hot stars the intensities of the bright lines decrease from $H\alpha$ toward shorter wave-lengths and the ultra-violet lines are frequently dark in the same spectrum in which $H\alpha$ is bright. Among the long-period variable stars at the lower end of the stellar temperature sequence the bright hydrogen lines are nearly monochromatic. In the titanium oxide variables their relative intensities are very different from those observed in the laboratory, $H\gamma$ and $H\delta$ being many times as strong as $H\alpha$ and $H\beta$. Since the temperatures (and presumably the pressures) are low it should be possible to reproduce these effects in the laboratory. A curious phenomenon in red stars is the decided weakness of $H\epsilon$ compared to $H\delta$ and $H\zeta$. This may be due to the absorption of calcium since $H\epsilon$ lies within the broad calcium line H. A definite laboratory problem is to find a condition in which calcium vapor is nearly opaque to the hydrogen line $H\epsilon$.

12. Indirectly excited fluorescence spectra. STANISLAW LORIA, California Institute of Technology.—Franck and Cario's experiments on fluorescence spectra of some metallic vapors mixed with mercury vapor and excited by radiation absorbed only by the latter, have been repeated with a result confirming the statements of previous observers. The spectrograms of Tl-fluorescence contain all lines recorded by Cario and also the lines 2922 ($4d_2-2p_1$), 2768 ($3d_2-2p_2$) and 2580 ($2s-2p_2$), which are to be expected theoretically but could not be found on Cario's plates. The investigation of the influence of inert gases on the intensity of "sensitized" fluorescence confirmed in general the results obtained by K. Donat (Zeits. f. Phys. **29**, 345, 1924); the admixed gas weakens the intensity of mercury lines but intensifies the fluorescence of the indirectly excited vapor. The effect is different for different lines. An attempt is being made to perform this last experiment under well defined conditions of pressure and temperature for all components of the mixture, so as to obtain data sufficient for the determination of the time during which a mercury atom may (under various conditions) persist in its metastable state.

13. The effect of minute surface impurities upon the photo-electric long wave-length limit of mercury. HUGH K. DUNN, California Institute of Technology.—The definite establishment by C. B. Kazda of a sharply measurable long wave-length limit for a perfectly clean surface of flowing mercury has rendered possible for the first time the determination of the effect of minute traces of impurities upon such a limit. In the present work the long wave-length limit of flowing mercury is again found at Kazda's value of 2735 A, with an uncertainty of not more than 10 A. The cleanest obtainable stationary surface of mercury has yielded, however, a value of 2860 A, the change from the first to the second values upon stopping the flow being strikingly reproducible. Certain types of impurities are found to push the limit down below the

2537 line. The effect of hydrogen impurity upon this limit has been especially investigated.

14. Secondary emission from nickel surfaces due to positive ion bombardment. A. L. KLEIN, California Institute of Technology.—The apparatus used consisted of a number of concentric nickel cylinders surrounding a central positive ion emitter. The cylinders are pierced with slots in such a manner that they act as grids, shields, and collectors. The observations were taken by running saturation curves for the various voltages of acceleration of the positive ions. The velocity of emission of the secondary electrons was obtained from the point of maximum slope of the saturation curve, and the amount of the emission from the saturation value. Secondary emission was obtained for primary velocities as low as fifty volts.

15. The ionization of hydrogen by electron impact as interpreted by positive ray analysis. T. R. HOGNESS and E. G. LUNN, University of California.—The method of positive ray analysis has been applied to the study of the processes of ionization of hydrogen by impact electrons. The results of experiments on the relative amounts of H^+, H_2^+ and H_3^+ ions as a function of the pressure, show that the only process occurring when an electron of sufficient energy collides with a hydrogen molecule is that represented by the equation:

$$H_2 = H_2^+ + e.$$

The H_2^+ thus formed is energetically unstable, and on collision with a neutral molecule disrupts to form H^+ and H; the H^+ may attach itself to a neutral molecule forming H_3^+. This conclusion has been verified by studying the ionization in mixtures of helium and hydrogen. The *ionization potential of hydrogen* was found to be 16.0 volts. In *mixtures of hydrogen and helium* the ion HeH_2^+ and one which is probably HeH_3^+ were observed in addition to H^+, H_2^+ and H_3^+. The bearing of the above conclusions upon the various interpretations of the ionization potentials and ionization processes is discussed. The discrepancy between the ionization potential calculated from the heat of dissociation and from theoretical ion models and that experimentally determined is pointed out.

16. Ionic mobilities in ether as a function of pressure. L. B. LOEB, University of California.—Mobilities of positive and negative ions were measured in ethyl ether as a function of the pressure using the Franck modification of the Rutherford alternating current method with a square wave alternating current. The mobility reduced to N.T. P. for positive ions was 0.19 cm/sec. at 340 mm pressure and rose to 0.22 cm/sec. at 5 mm pressure. The latter value was the same as that for the negative ion at 340 mm which was 0.223 cm/sec. Thus the positive ion in ether shows the two types of mobility observed by Erikson (Phys. Rev. **20**, 117, 1922; **24**, 622, 1924) and Wahlin (Phys. Rev. **20**, 267, 1922; Proc. Nat. Acad. Sci. **10**, 475, 1924), new ions having a mobility equal to that of the negative and aged ones having a lower value. The age of the high mobility ions was about .001 sec.; that of the low .02 sec. Below 80 mm the negative mobility rose rapidly because of the effect of electrons that had not formed ions, dual curves of the type observed by Wellisch (Phil. Mag. **34**, 199, 1917; Am. Jour. Sci. **44**, 1, 1917) for such ions being found at 40 mm. Great care must be used in deducing mobilities from such curves because of the smooth asymptotic feet of the curves caused by the gauze and auxiliary field. Care must be taken to avoid changes in mobility produced by changes in the value of the auxiliary field alone.

17. The theory of the range of α-particles. EDWARD CONDON and L. B. LOEB, University of California.—The theory of the range of α-particles which has been developed by Henderson (Phil. Mag. **44**, 680, 1922), discussed by Fowler (Proc. Cambr.

Phil. Soc. **21**, 521, 1923), and tested by Bates on rare gases (Proc. Roy. Soc. **A106**, 622 1924) leads to the equation

$$-MVdv/dx = (8\pi e^4 N/mV^2)\Sigma n_s \log(2mV^2/T_s)$$

for the rate of loss of energy of an α-particle along its path. Here n_s is the number of electrons having the ionization potential T_s. This paper points out two errors in the argument leading to this equation. (1) The assumption is tacitly made that multiple ionization in a given shell can take place with the same ionization potential as single ionization from the same shell. (2)The calculation also assumes that processes will happen in the atoms of the gas corresponding to multiple ionization of the gas by single impact. This is in direct contradiction with the results of Millikan's studies of ionization by α-particles, except in the case of helium. It is shown that the effect of making these corrections to the theory is to increase the existing discrepancy between this theory and experiment, indicating that this line of attack on the problem is inadequate.

18. Conductivity of gases during chemical reaction. A. KEITH BREWER, California Institute of Technology.—In preceding papers it has been shown that when gas phase reactions were allowed to take place between gold or platinum electrodes a current was detected which was proportional to the quantity of material reacting and to the applied voltage over the field investigated (0 to ± 2700 volts per cm). It has since been shown that a conductance is observed when various oxidizable vapors are mixed with oxygen at temperatures well below that of the ignition temperature. The temperatures at which the conductance begins fall in about the same order as the ignition temperatures. In each case the conductance increases exponentially with the temperature; on the average the conductance doubles for a rise in temperature of 10°C. Experiments are presented to distinguish between reactions taking place on the surface of the electrodes, and reactions throughout the body of the gas.

19. Remark on the dielectric constant of gases. PAUL S. EPSTEIN, California Institute of Technology.—The recent measurements of A. Glaser (Ann. der Phys. **75**, 459, 1924) show that the diamagnetic susceptibility of gases varies as a function of the pressure and of the magnetic strength of field. The theoretical explanation of this effect is not quite known. On the other hand, the theory of the action of an electric field presents no difficulties and it is possible to predict an analogous change of the dielectric constant with the strength of field. For monatomic hydrogen we can carry through the computations completely. For weak and normal electric fields the dielectric polarization is considerably higher than for extremely high values of the strength of field. This drop is due to the gradual development of the Stark effect leading to a change of the orbits and to an orientation of the atoms in the direction of the field.

20. Electrolysis through glass as a sodium voltameter. R. C. BURT, California Institute of Technology.—An electric light bulb is immersed (with filament lighted) in molten sodium nitrate, and sodium is driven electrolytically through the glass wall. From the weight of sodium thus deposited and the time integral of the current, Faraday's laws are checked, it is believed, to 0.2 per cent. Further experiments are in progress to verify this more precisely. This makes available another form of voltameter.

21. The theory of the radiometer. H. E. MARSH, E. CONDON and L. B. LOEB University of California.—In a recent number of the Zeits. f. Phys. (**27**, 1, 1924) there appeared an article by A. Einstein in which the radiometric pressure observed on vane radiometers where the pressure is such that the mean free path is less than the dimensions of the vane, is ascribed to a region of the vane along its edges of width of the order of a mean free path at that pressure. If this theory is correct it should be expected that the determining factor in the operation of such radiometers depends on the length of the

edge of the vane rather than the total area of the vane as hitherto supposed. This was tested experimentally by constructing two types of vanes whose areas and area moments were equal on two sides of a vertical axis but in which the edge moments on one side were four times as great as they were on the other. On placing such vanes in a uniform beam of light it was found that the side of the vane having the greater edge moment was universally more strongly acted upon than the other side. The effect however was not nearly as great as theoretically anticipated from the ratio of the edge moments. The deviation was ascribed to the greater cooling produced on the vane having the larger edge moment. On a thicker vane where this effect was assumed to be minimized results more nearly in quantitative accord with the theory were observed.

22. Adaptation of the phonelescope as a precision pitch indicator, and an application as a detector of pitch variation in vocal tones. L. E. DODD, University of California, Southern Branch.—By permitting the vibrating beam from the phonelescope to fall upon a suitable stroboscopic screen in motion, an immediate direct indication of the frequency of the beam and of the constancy of this frequency, is obtained. The test is an objective one, since the detection of pitch, particularly of pitch variation, is not dependent upon the ear, but upon the eye, so that change in loudness or in quality of the tone cannot possibly be interpreted as a pitch wandering, or conversely, a pitch wandering cannot possibly be interpreted as a variation of intensity or of timbre. The particular practical application was to test the effect upon pitch, of external local pressure gradually applied to the throat at different designated points during the sounding of a vocal tone by the subject. Under such circumstances variations in pitch, either upward or downward depending upon the place where the pressure was applied, and often great enough to be detected easily by ear, were obtained. Such data are of value in a physiological study of the action of the muscles controlling the vocal cords. In the cases of more pronounced pitch change, the method always served as an objective confirmation of the evidence by ear, and in all cases it constituted the sufficient test of a pitch change.

23. The interfering effect of tones and noise upon the quality of speech in an auditorium. V. O. KNUDSEN, University of California, Southern Branch.—Speech-articulation tests are being conducted to determine the effect of noise upon the quality of speech in an auditorium. The tests are conducted in a quiet room, having a volume of 15000 ft^3 and a time of reverberation of 1.3 seconds. Tests with pure tones as the interfering disturbance, indicate that tones of low and medium pitch, below 2000 d.v., produce a greater interference than tones of high pitch. Thus, tones of 256 d.v. and 4096 d.v., each having an energy equal to 10^6 times the energy for its minimal audible tone, reduced the word, vowel, and consonant articulations to 45, 81, and 69 percent and 80, 98, and 89 percent, respectively. This is consistent with the data of Fletcher, Wegel and Lane on the auditory masking of one tone upon another. Low tones disturb both vowels and consonants, whereas high tones disturb only the consonants. Tests on typical hard of hearing individuals who claim that in the presence of a noise they hear better, indicate that they actually hear not as well.

24. A recording acoustic marine depth-sounder. LEO P. DELSASSO, University of California, Southern Branch (introduced by J. M. Adams).—Preliminary tests were conducted aboard a U. S. battleship during a full-power run, to investigate the disturbing effect of incidental noises and to compare the waves direct from the source with those reflected from the bottom, as to intensity and form. The oscillograms obtained indicate a wide variation of the echo in both respects over various bottoms. The results of these tests made it possible to complete a mechanism which by a selective multistage amplifier records the time of transit of a sound wave from the source to the bottom and back,

on a paper chart. Tests with this recorder aboard the U. S. S. Maryland indicate that, with few modifications, it should be possible to record automatically on the bridge of a ship all depths that will contribute to her navigation.

25. New evidence for a sharply bounded and very rigid core in the earth. JAMES B. MACELWANE, University of California.—The existence of a clearly defined shadow zone on the surface of the earth and therefore of a sharply bounded, refracting core within, as maintained by Wiechert and Gutenberg and denied very generally outside of Germany, is proved conclusively by the seismographic records of the South Pacific earthquake, June 26, 1924. The energy of the direct longitudinal group of waves is very great at all stations up to arcual distances approaching 103°, but beyond this point becomes almost zero. At 142° a second longitudinal group which appears in this shadow zone begins to increase slightly in amplitude and at 144° becomes very large indeed. The rigidity of the deep interior has been denied by Knott and others on the basis of absence of shear waves. Transverse waves transmitted by the core seem to be present on the records of this earthquake at many stations from an arcual distance of 132° onward. Their speed is such as to make Poisson's ratio in the core approximately $\sigma = \frac{1}{4}$. In that case the core is very rigid and the density increases suddenly at the boundary.

26. The relative importance of wind, humidity, and solar radiation in determining evaporation from lakes. N. W. CUMMINGS, California Institute of Technology.—Hourly determinations were made of evaporation and temperature of the water contained in a Dewar jar 15 cm in diameter and approximately 25 cm deep. Simultaneous determinations of radiation from sun and sky were made with a copper disk pyranometer. The jar was packed in sawdust and it had previously been found that the rate of leakage of heat through the walls for one degree difference in temperature was extremely small. The radiant energy per square centimeter integrated over any time interval was equal to the heat represented by the change in temperature of the water plus the heat represented by the evaporation per square centimeter during the same time interval, plus a relatively small correction to be determined empirically. This correction appears to depend on atmospheric conditions.

27. Dynamical Einstein space-times which contain a conformal-euclidean three-space. H. P. ROBERTSON, California Institute of Technology.—The manifolds here examined are those having a line element of the form $ds^2 = f(dx^2+dy^2+dz^2) - gdt^2$ where f and g are functions of x, y, z, and t. The problem of the integration of the cosmological equations for such fields is found to involve the integration of sets of first order equations which are linear and homogeneous in the derivatives. One of these sets is not completely integrable, but particular integrals are found. The space coordinates being isotropic the fundamental velocity is the same in all directions from each point. The interpretation of the solutions is as yet incomplete, but among those that have been interpreted are found theorems like the following: If "stationary" observers in such a manifold find that their proper-time does not depend on their position in space, then space-time is itself conformal-euclidean, i. e. a hypersphere.

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